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Current Status, Research Needs, and Opportunities in Applications of Surface Processing to Transportation and Utilities Technologies

Proceedings of a December 1991 Workshop

A.W. Czanderna and A.R. Landgrebe,
Editors

- Executive Summary
- Assessment of the Current Status in Surface Characterization
- Assessment of the Current Status in Surface Modification
- Discussion of Research Needs and Opportunities for Advancing Transportation and Utilities Technologies Through Applied Surface Science and Surface Processing

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SUMMARY

Surface Processing is a subset of applied surface science for (1) preparing tailor-made surfaces for specific end-use applications, (2) characterizing the surfaces, and (3) developing a theoretical framework. These proceedings document the principal discussions and conclusions reached at a workshop held on December 10–12, 1991, and cosponsored by the U.S. Department of Energy (DOE), Office of Transportation Technologies and Office of Utility Technologies; and the National Renewable Energy Laboratory (NREL) under contract to DOE. The proceedings document eight chapters about the current status of surface characterization with a principal focus on the composition, structure, bonding, and atomic-scale topography of surfaces. The proceedings also document eleven chapters about the current status of surface modification and include a summary of techniques—electrochemical, plasma-aided, reactive and nonreactive physical vapor deposition, sol-gel coatings, high-energy ion implantation, ion-assisted deposition, organized molecular assemblies, and solar energy. Three brief chapters in the Appendices document basic research in surface science by the National Science Foundation, the Air Force Office of Scientific Research, and the Division of Materials Sciences, Office of Energy Research, DOE that underpins surface processing.

The purposes of the workshop were to bring together scientists and engineers from academia, industry, and federally funded laboratories to form working groups with a mixture of expertise in surface characterization and surface modification, and to identify and prioritize the research needs and opportunities of each of 10 different topical areas of applied surface science as they relate to applications in the transportation and utilities technologies. Each participant was invited to serve on one of 10 working groups concerned with a topic in applied surface science. The topics were corrosion protection, solid batteries and fuels cells, lubricating and wear surfaces, polymer/metal (oxide) interfaces, thin-film multilayer solar collectors, accelerated life testing of devices with solid/solid and solid/liquid interfaces, interfacial microchemical characterization, conducting polymers, photoelectrochemical systems, and modification with organized molecular assemblies. The participants identified generic and specific problems at materials interfaces in the 10 topical areas and conceived stimulating ideas on research and development that focus materials and systems with targeted end-use applications. With these proceedings, researchers and technologists can be exposed to the topical areas and deliberations of the workshop.

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PREFACE

These proceedings document the principal discussions and conclusions reached at a workshop held December 10-12, 1991, and cosponsored by the U.S. Department of Energy (DOE), Office of Transportation Technologies and Office of Utility Technologies; and the National Renewable Energy Laboratory (NREL) under contract to DOE. The purposes of the workshop were to bring together scientists and engineers from academia, industry, and federally-funded laboratories to form working groups with a mixture of expertise in surface characterization and surface modification, and to identify and prioritize the research needs and opportunities of each of 10 different topical areas of applied surface science as they relate to applications in the transportation and utilities technologies.

Surface Processing is a subset of applied surface science for (1) preparing tailor-made surfaces for specific end-use applications, (2) characterizing the surfaces, and (3) developing a theoretical framework. Participants were sent current-status, "plenary" summaries of the state of the art in the relevant methods for surface modification and surface characterization prior to the workshop. They were also sent documents that indicate the crucial importance of surface properties for applications in conservation and renewable energy technologies, energy distribution, energy generation by utilities, and buildings, and by other industrial energy users. At the workshop, overview lectures on surface processing in the transportation industry by Dr. D. Schuetzle of the Ford Motor Company and surface processing opportunities in the utility industries by Dr. R. McConnell of NREL. The current status summary papers are contained in Chapters 1 through 8 for surface characterization and Chapters 9 through 19 for surface modification.

Each participant was invited to serve on one of 10 working groups concerned with a topic in applied surface science. The topics were corrosion protection, solid batteries and fuels cells, lubricating and wear surfaces, polymer/metal(oxide) interfaces, thin-film multilayer solar collectors, accelerated life testing of devices with solid/solid and solid/liquid interfaces, interfacial microchemical characterization, conducting polymers, photoelectrochemical systems, and modification with organized molecular assemblies.

The participants identified generic and specific problems at materials interfaces in the 10 topical areas and conceived stimulating ideas on interfacial R&D that focus materials and systems with targeted end-use applications. With these proceedings, researchers and technologists can be exposed to the topical areas and deliberations of the workshop. The needs and opportunities for surface processing R&D are identified and discussed in Chapters 20 through 29.

Basic research in surface science is well funded by several federal agencies including the DOE Office of Energy Research, the Division of Materials Sciences (OER/DMS), the National Science Foundation (NSF), the Air Force Office of Scientific Research (AFOSR), the Office of Naval Research (ONR), and to a lesser extent, the Army Research Office. All these agencies were invited to summarize their activities for the participants. Relevant summaries of the activities of OER/DMS, NSF, and AFOSR are contained in Appendices A1 through A3, and representatives from OER/DMS and NSF participated in the working groups.

Acronyms and abbreviations (AAA) used throughout this document are given in a Glossary on pages A4-1 through A4-3. Acronyms and abbreviations are also defined in each chapter with their initial use, but tables of AAA were generally eliminated from each individual chapter. The participants' addresses and phone numbers are given on pages A5-1 through A5-6.

The editors express their deep appreciation to all participants for their analytical, creative, and incisive involvement. We especially thank the authors of Chapters 1 through 19 and the (co)chairmen of the working groups corresponding to Chapters 20 through 29 for their cooperation and efforts in producing and/or coordinating the preparation of the written copy. We also gratefully acknowledge NREL staff members for their significant administrative, coordinating, editing, and word processing contributions—Julie Baxes and Dori Nielsen, Conferences Group; Janet Fried, Pat Haefele, and Fran VanDerPol, Word Processing Group; Barbara Spitz, Corporate Communications Section; and Regina Witherspoon, Measurements and Characterization Branch; for their help before, during, and after the workshop.

EXECUTIVE SUMMARY

A.W. Czanderna and A.R. Landgrebe

The goal of surface processing is to develop and use innovative methods of surface modification and characterization that will provide optimum performance and environmental protection for cost-effective operational lifetimes of systems, materials, and components used for specific applications in the transportation and utilities technologies.

Chemical and/or physical effects at surfaces determine the performance and the lifetime of devices in a variety of technologies. This fact has become apparent in the last two decades as new techniques have allowed us to characterize surfaces at the atomic/molecular level with a great degree of sensitivity. The ability to control the modification of surfaces and tailor-make surfaces for specific applications has also improved significantly in the same period. Major advances have also been made in the theoretical understanding of surface phenomena and the ability to model surface processes. These advances led to the possibility of developing model systems to predict surface properties. The study of these phenomena has spawned a new field of research that is commonly referred to as surface science.

Basic surface science research is well funded by several federal agencies, including the National Science Foundation, the Office of Naval Research, the Air Force Office of Scientific Research, and DOE's Division of Basic Energy Sciences, especially by the Division of Materials Sciences. Several research centers have been created. The Center for Advanced Materials at Lawrence Berkeley Laboratory and the Center for Surface and Interface Research at the University of Connecticut are typical examples. Furthermore, the Division of Materials Sciences has a long history of generously funding surface science research at Lawrence Berkeley Laboratory, Ames Laboratory, Argonne National Laboratory, Oak Ridge National Laboratory, and Brookhaven National Laboratories, but has provided minimal funding for mission-oriented laboratories (e.g., Sandia National Laboratories, Los Alamos National Laboratory, Lawrence Livermore Laboratory, and National Renewable Energy Laboratory). In addition, federal research laboratories, such as the Naval Research Laboratory, and several universities have developed strong capabilities in basic surface science research.

Surface processing is a subfield of applied surface science for preparing tailor-made surfaces for specific end-use applications, characterizing the surfaces, and developing a theoretical framework. The crucial importance of surface properties is well known for applications in conservation and renewable energy technologies, energy distribution, energy generation by utilities, and buildings, and by other industrial energy users [1]. The unique aspects of these applications areas provide surface scientists and engineers with unusual opportunities to carry out focused research and development on materials/systems with targeted end-use applications. In the transportation technologies, for example, the efficiencies, performance, and lifetimes for electrochemical storage and distribution, and surfaces for lubricating and wear depend very much on the surface properties of the active materials. The ability to tailor-make surfaces for specific applications will have tremendous impacts on these technologies. Concurrently, being able to monitor the changes on these surfaces and characterize the chemical and physical processes occurring on them will allow us to understand the underlying phenomena in microscopic detail and to develop improved materials and surfaces for these applications.

Applications of surface processing include a broad spectrum of energy technologies. All conservation and renewable energy technologies will benefit from surface processing research and development. The National Materials Advisory Boards panel on corrosion estimated a potential savings of several billion dollars annually if surface processing technologies can reduce corrosion problems. Additional billions can be saved if interface reactions that degrade device and component performance can be slowed or essentially eliminated. The lifetime of our aging power generation facilities will also be extended as new materials and surfaces are defined by responding to the opportunities for research and development identified in this document.

Information on the current status of surface characterization and surface modification is contained in Chapters 1 through 8 and Chapters 9 through 19, respectively. Progress in surface characterization and modification has been spectacular since the early 1970s. Needs and opportunities in 10 topical areas of applied surface science are contained in Chapters 20 through 29.

I. OVERVIEW OF SURFACE PROCESSING AND INTERFACIAL PHENOMENA WITH SPECIFIC APPLICATIONS IN THE TRANSPORTATION AND UTILITIES TECHNOLOGIES

The essential technical knowledge underpinning the need for a surface processing research and development is:

- Surface processing combines surface characterization and modification into an applied surface sciences subset of surface science.
- Essential components and systems in the conservation and renewable energy technologies consist of using surfaces or thin-film multilayers.
- Surfaces/interfaces are thermodynamically unstable and ultimately determine the lifetime of systems, materials, and components in conservation and renewable energy technologies.
- The rate of reaction at unstable interfaces must be slowed to achieve the desired lifetime while maintaining performance.
- Surface modification may be successful in slowing reaction rates.
- Surface characterization of compositional, bonding, structural, and topographical changes that often precede degradation are essential for monitoring the reaction rate.

A. Surface Characterization

Recent developments have provided the means for surface characterization with unprecedented resolution. The variety of techniques all provide some aspect of the information required, and usually a combination of techniques is required to explore a particular surface process to obtain a thorough understanding of the particular phenomenon. Some of these techniques are labeled ex situ, meaning that the sample needs to be removed from its operating environment into a specialized high vacuum chamber for analysis. In some applications, questions arise concerning the extent to which the surface is modified as it is removed from the operating conditions, and careful control of the transfer process becomes essential for proper interpretation of the data. Other techniques are labeled in situ, because the surfaces can be characterized in their operating environments. Usually, both types of characterization techniques are essential for a thorough understanding of a particular surface phenomenon. The promising surface characterization techniques include microscopies for surface structure (high resolution electron microscopy, analytical electron microscopy, transmission electron microscopy, scanning tunneling microscopy, atomic force microscopy, low energy electron diffraction, and ion scattering spectroscopy), compositional surface analysis using ion (secondary ion mass spectrometry, secondary neutral mass spectrometry, surface analysis by laser ionization, ion scattering spectroscopy, Rutherford backscattering spectroscopy, and nuclear reaction analysis) and electron (X-ray photoelectron spectroscopy, Auger electron spectroscopy, scanning

Auger microscopy, ultraviolet photoelectron spectroscopy, and core-electron energy loss spectroscopy) spectroscopies, vibrational spectroscopies for chemical bonding (Fourier transform infrared-reflection absorption spectroscopy, Raman, high resolution electron energy loss spectroscopy, surface enhanced Raman spectroscopy, inelastic electron tunneling spectroscopy, and optical spectroscopic ellipsometry) and synchrotron radiation methods (extended X-ray fine structure spectroscopy, surface extended X-ray fine structure, and X-ray absorption near edge structure) for local bonding and ordering. Summaries of the current status of the most important techniques above are contained in Chapters 1 through 8.

B. Surface Modification Techniques

The techniques commonly used to modify or protect a surface include coatings, physical treatment, and chemical modification. A variety of techniques are used to accomplish the treatment process in each of the three categories, as discussed below.

Coatings technologies can be subdivided into polymer coatings and metal and ceramic coatings. A wide variety of organic polymeric coatings can be applied to surfaces. The preparation of a surface prior to the application of any coating is critical, especially with organic coatings. The techniques for application include brushing and spraying, electrostatic spraying and electrochemical deposition, and coating with organics that are then cured to produce the protective layer.

A wide variety of high- and room-temperature processes are used in the preparation of metallic and ceramic (including glassy) types of coatings. The room-temperature coating processes include:

- Electrochemical and electroless deposition of metallic coatings; pulsed electrodeposition of metallic glasses
- Ion plating, which involves the deposition of vapor-phase ions at electrically charged surfaces to produce metallic and alloy coatings
- Chemical vapor deposition, which involves chemical reactions of vapor-phase species to produce metals, alloys, and other chemical compounds, including ceramics
- Evaporation and sputtering, which involve the deposition of materials and the combination of materials by physical vapor transport.

Chemical vapor deposition, evaporation, and sputtering can also be conducted at high temperatures. In addition, techniques specifically conducted at elevated temperatures include solar furnace processing, laser-assisted spraying and annealing, spray and detonation gun coating, and sol-gel coating.

Physical treatments modify the surfaces physically using mechanical techniques, which include either shot peening or shock hardening. Photon (solar furnace or lasers) or electron beam processing involves the rapid scanning of a surface with a high-power photon source or electron beam. In the latter cases, a thin molten surface layer is produced and rapidly solidified by heat transfer, thus producing metastable surface alloys and glassy alloy surface layers.

Chemical surface modification is usually accomplished with one of three approaches. These include:

(1) Chemical reactions at the surface, in which the surface composition is changed by reaction with a gaseous species, usually at an elevated temperature. Nitriding and carbiding are examples of such treatments, in which a surface phase is produced whose thickness is determined by diffusion.

(2) Electrochemical surface modification, which involves an electrochemical reaction to produce a modified surface. Typical examples include the electrochemical formation of polypyrrole films and the attachment of silane-type ligands.

(3) Ion implantation, which involves the implantation of high-energy ions into the near-surface region. This produces new metastable surface compositions, usually without causing dimensional changes.

In addition to the above well-known techniques, there are chemical approaches in which the adsorption of organic species in organized molecular assemblies improves the corrosion resistance. How these inhibitors actually work is not very clear, and the whole effort is more of an art than a science. Understanding the attachment chemistry of organized molecular assemblies onto inorganic surfaces and the state of organization of organized molecular assemblies could assist us in developing another powerful technique to modify specific surface properties.

II. NEEDS AND OPPORTUNITIES FOR USING SURFACE PROCESSING WITH SPECIFIC APPLICATIONS TO TRANSPORTATION AND UTILITY TECHNOLOGIES

A. Scope

The scope of the research and development needs and opportunities in surface processing can be grouped quite naturally into three areas:

- Surface Processing Applications for Transportation Technologies.
- Surface Processing Applications for Utility Technologies.
- Generic Applications of Surface Processing.

Research and development in these three areas do overlap, as evidenced by the 10 subjects considered at the workshop. These subjects and the principal technology applications areas are: corrosion protection, fuel cells and solid batteries, lubricating and wear surfaces, and photoelectrochemical systems for surface processing applications for transportation technologies; polymer/metal(oxide) interface needs and thin-film, multilayer solar collectors for surface processing applications for utility technologies; and accelerated life testing of systems, materials, and components with solid/solid, solid/liquid, and solid/gas interfaces, interfacial microchemical characterization needs, conducting polymers in energy technologies, and organized molecular assemblies for generic applications of surface processing.

Other study areas could have been included in which surface properties are important, e.g., catalysis, coatings, adhesives, glass technologies, and low-energy surfaces such as diamond-like or silicon carbide films. Except for catalysis, these study areas are included as subsets of aspects of the 10 subjects given previously.

B. SURFACE PROCESSING NEEDS AND OPPORTUNITIES FOR SURFACE PROCESSING APPLICATIONS FOR TRANSPORTATION TECHNOLOGIES, SURFACE PROCESSING APPLICATIONS FOR UTILITY TECHNOLOGIES, AND GENERIC APPLICATIONS OF SURFACE PROCESSING

The technical approach for using surface processing includes identifying the degradation mechanisms in candidate system, material, and component configurations primarily from experimental work that simulates conditions of use, and interpreting the data to deduce the mechanisms of degradation. The Reliability Research Group at AT&T Bell Laboratories has successfully used this approach for more than 15 years. As the degradation mechanisms are understood, the materials and/or use configurations will be modified as needed, or new materials options will be sought and recommended. The work in any applied science area must be weighted toward finding the limiting factors for a cost-effective, service lifetime, i.e., the fastest degradation processes will be studied first and most intensively, and when those degradation problems have been corrected, research will be focused on the next limiting issue(s). The correlation between accelerated aging and lifetime prediction must necessarily be accomplished with results from the other study areas. In each of the 10 topical areas of applied surface science listed below, key research issues are indicated.

1. Corrosion Protection

There are major application areas for corrosion protection in the transportation industries, particularly the application of paint on metals and plastics (see also II. B. 4., below). Examples include galvanized steel, external mirrors, headlamps, trim, hood and door hem flanges, tailgate assemblies, and bumpers. Surface modifications may be achieved by using high-energy processes, zinc protective layers, sol-gel films, or alodine conversion coatings.

Key research issues are to:

(1) Improve galvanizing alloys on steel.

(2) Improve adhesion of protective layers (e.g., paint).

(3) Improve the understanding of light metal alloy corrosion systems and reduce the corrosion rate of the protected metal.

(4) Identify cleaning processes that precede surface modification in (e).

(5) Select surface modification methods for achieving (b) and (c) (e.g., anodic oxide films, phosphate conversion coatings, electrodeposition, and sol-gel coatings).

(6) Use in situ microchemical characterization of buried interfaces in light-alloy systems, electrochromic windows, and photovoltaic modules to establish chemistry, morphology, mechanical stress, and mechanisms of degradation.

(7) Establish compatibility and retarded degradation after (5).

(8) Measure accurately the interfacial adhesion by a physical process.

(9) Assess the relative contribution of chemical versus physical bonding to surface adhesion.

(10) Develop methods for homogeneous modification of irregular shapes.

(11) Perform research and development on those surface processing methods with potential for use on a manufacturing scale with on-line process control.

Corrosion protection is also required in batteries and fuel cells, in mirrors for concentrating solar radiation (e.g., the Ag/polymethylmethacrylate interface), in photovoltaic cells (e.g., metallization, busline, and interconnects), and in electrochromic devices. The research needs are considered below in Sections II. B. 2. and II. B. 5., respectively. Other corrosion problems considered to be of lower priority include the compatibility of working fluids in solar thermal systems, biofouling in ocean thermal systems, corrosion of ceramics, glasses, and sensors, and corrosion in fuel systems.

2. Solid Batteries and Fuel Cells

The major application area for solid batteries and fuel cells is in the transportation industry for the electric vehicle program. Overlapping exists with corrosion protection (e.g., carbon and graphite), polymer/metal(oxide) interfaces (e.g., lithium batteries), conducting polymers (e.g., electronic and ionic), microchemical characterization (surface composition and microstructure of pores), and catalysis.

Because no generic examples exist for all battery/fuel cell systems, model systems identified for study include polymer electrolyte membrane fuel cells, direct methanol fuel cells, zinc/air batteries, and lithium/polymer batteries. The key research issues, which are related to catalysis, corrosion, electronic/ionic contact, and hydrophobic/hydrophilic behavior at the solid/boundary interface, are to:

(1) Define or identify the interfacial function, desired properties, and specific problems.

(2) Identify the surface modification needed to solve the problem.

(3) Identify the in situ characterization needed to elucidate reaction mechanisms and degradation mechanisms.

(4) Conduct durability testing on the modified fuel cells/batteries.

3. Lubricating and Wear Surfaces

The major application areas for lubricating and wear surfaces are in the transportation (e.g., engines, fuel delivery systems, valve trains, and power transmissions), metal forming, and foundry industries. The key research issues are to identify surface modifications (e.g., nitriding, ion implantation, plasma processing, phosphating, and sol-gel coatings) to:

(1) Reduce wear in valve guides/stems and piston ring/liners systems.

(2) Reduce wear in power gears/bearings and clutch materials.

(3) Reduce wear on cam rollers and journal bearings.

(4) Reduce wear on injector plungers, spray holes, and plunger tips.

(5) Improve cylinder kits and fuel pumps for alternate fuels.

(6) Reduce wear on lightweight materials.

(7) Improve the surface finish on composites.

(8) Reduce the wear on nonferrous forming tools, ferrous forming dies, and aluminum foundry patterns.

(9) Model wear and adhesion between moving parts.

4. Polymer/Polymer and Polymer/Metal(Oxide) Interfaces

The principal applications areas for polymer/polymer and polymer/metal(oxide) interfaces are in the utilities technologies (e.g., photovoltaic, solar thermal, power transmission, windows, and wind turbines), although significant applications exist in the transportation technologies. For practical purposes, polymer/metal interfaces is a misnomer except for polymers on gold. Even the noble metals (e.g., silver, platinum, and iridium) have a monolayer of oxidized surface in practical use, and this oxidized monolayer or multilayers (e.g., aluminum, copper, and iron) will dictate the interface behavior. The interphase regime is better nomenclature as it indicates the material in the region between two different solid phases.

The key research issues are related to painted metal or plastics; adhesively bonded components; electronic devices including photovoltaic modules, sensors, and microelectronics; and metallized polymers such as mirrors to reflect solar radiation. The issues are to:

(1) Select materials in the design stages for recyclability, compatibility, processibility, and performance.

(2) Select the optimal surface modifications (e.g., cleaning, vapor deposition, adhesion promoters, plasma treatments, and ion implantation) for each specific materials system.

(3) Understand polymer coating formation methods.

(4) Elucidate interphase formation mechanisms.

(5) Elucidate interphase degradation mechanisms.

(6) Characterize surfaces and the interphase (morphology, composition, bonding, and structure).

(7) Develop in situ in-process monitors for large scale production.

(8) Develop nondestructive testing methods for assessing the adhesion strength.

(9) Perform accelerated aging as screening tests and then to establish degradation mechanisms and make lifetime predictions.

(10) Establish tolerance in processing treatments that will still yield adequate quality of the interphase.

5. Thin-Film, Multilayer Solar Devices

The principal application areas for thin-film, multilayer solar devices are for the utilities technologies from photovoltaic, solar thermal, and solar buildings (i.e., electrochromic windows). Surface modification methods (e.g., plasma deposition and rapid thermal annealing) are again component- or device-specific and must be chosen as part of the research program. Most of the key research issues have been delineated in DOE/NREL 5-year program plans or initiatives related to these technologies. These issues are to:

(1) Identify interface degradation mechanisms that limit device lifetime or reduce the performance.

(2) Improve the durability of encapsulated photovoltaic devices by lowering the rate of degradative interface reactions (e.g., metallization corrosion, surface-catalyzed pottant degradation, environmentally tight edge seals).

(3) Improve the durability of silvered polymers by eliminating polymer/silver interface corrosion.

(4) Develop thin-film photovoltaic modules with improved junction properties to raise the voltage and fill factors.

(5) Improve the durability of electrical contacts in general, and specifically for cadmium telluride thin-film modules.

(6) Develop low-energy, antisoiling surfaces for mirrors, photovoltaic modules, and electrochromic windows.

(7) Improve photovoltaic and electrochromic window materials to minimize interface charge-carrier trapping effects.

(8) Devise diffusion barriers to minimize problems resulting from interdiffusion at interfaces.

(9) Modify surfaces to enhance adhesion in multilayer stacks.

(10) Modify semiconductor/metallization interfaces to obtain long-term stability, high performance, and corrosion resistance.

(11) Develop deposition processes that eliminate the need for extractive patterning processes.

(12) Identify surface processed interphases that eliminates mechanical stresses between thin film multilayers.

(13) Conduct accelerated life testing, establish degradation mechanisms, and estimate service lifetimes for photovoltaic, solar thermal, and electrochromic window devices.

(14) Improve glass surfaces with and without deposited thin films for stability.

(15) Reduce metallization patterning costs by using a solar furnace.

6. Accelerated Life Testing

The application areas for accelerated life testing certainly include all utilities and transportation technologies, but the areas are as broad as industry itself. Surprisingly, the current status is almost universally dependent on the single point method of:

$$t_f(\text{real time, outdoors}) = kt_f\ (\text{failure in accelerated test}) \qquad (1)$$

where k is really thought to be a constant.

The key research issues are to:

(1) Identify critical accelerating stresses including the maximum allowable stress before a mechanism change occurs and the range of the stress as it relates to reality.

(2) Expand the use of the Spearman rank correlation method.

(3) Identify new approaches to relating lifetime prediction from failure in accelerated test, including defining what is a failure (e.g., percent of performance loss, change in appearance).

(4) Develop predictive models based on mathematical models, correlation methods, and data analysis, and compare them with results from large quantities of samples stressed to failure.

(5) Understand degradation mechanisms that lead to failure, depending on the variable (time, temperature, ultraviolet, relative humidity, water, etc.) and their synergism.

(6) Quantify real-time stresses versus accelerated test stresses to establish the simplicity or complexity of k in Equation 1.

(7) Educate personnel and their managements on the limits of accelerated life testing.

(8) Define how stresses are characterized and/or measured.

(9) Develop and consolidate data bases, especially for solar exposures in hostile terrestrial environments.

(10) Use extensive characterization of materials/interfaces to explain degradation mechanisms.

7. Interfacial Microchemical Characterization Needs

As the surface characterization component of surface processing, the interfacial microchemical characterization needs are applicable to all components of conservation and renewable energy technologies wherever an interface is present. The limiting stability of any system or component is the thermodynamically unstable interface. The current status of present methods has been summarized in Chapters 1 through 8. The crucial key research issues are to:

(1) Improve chemical specificity to detecting bonding, organic materials, and hydrogen.

(2) Develop real time techniques for use in on-line dynamic processing steps.

(3) Improve/develop new techniques (e.g., atomic force microscopy/scanning tunneling microscopy, X-ray optics, greater spatial resolution), especially for nondestructively studying real and buried interfaces, impurities at solid/solid interfaces, surface contaminants, interdiffusion, and interface and thin-film stability (degradation).

(4) Expand the availability of sophisticated measurements and analysis experts through collaboration, sharing, and more efficient use among universities, industry, and national laboratories.

(5) Improve detectability of defects, microtopography, and microphase formation.

(6) Extend more surface science techniques to characterizing the solid/liquid interface.

(7) Improve the monolayer sensitivity of Fourier transform infrared-reflection absorption and optical spectroscopic ellipsometry.

8. Conducting Polymers

The principal application areas for conducting polymers in the transportation technologies are in fuel cells, solid batteries, sensors, variable transmission windows and reflectors, and fuel tank surfaces (to prevent static charge buildup). In the utility technologies, applications/areas include supercapacitors, electromechanical actuators, electromagnetic shielding, photon-based optoelectronic devices, sensors and displays, and thin-film, high-temperature superconductor multilayer stacks. The key research issues are to:

(1) Understand the role of the interface in both electronic and ionic conduction mechanisms.

(2) Improve achievable electrical conductivity without decreasing the ease of processability.

(3) Obtain improved environmental and thermal stability.

(4) Minimize interfacial resistance between polymer electrolyte films and electrode materials.

(5) Develop processing procedures for application to various materials.
(6) Improve cycle life and cycle rate limitations at the polymer electrolyte/electrode interface.

(7) Optimize polymer synthesis on substrates and subsequent modification to obtain desired performance.

(8) Develop optically transparent conducting polymers.

(9) Improve adhesion between conducting polymers and various substrates.

(10) Fabricate polymers with improved physical properties such as tensile strength and flexibility.

9. Photoelectrochemical Systems

The principal application areas for photoelectrochemical systems can be in the utility or transportation technologies depending on the design of the particular photoelectrochemical system. The photoelectrochemical system may be constructed to yield electricity or a fuel, or to charge a battery. The key research issues are to:

(1) Obtain more fundamental understanding of the interface issues to facilitate identifying the optimal surface modification methods.

(2) Optimize long-term stability and improved efficiency of the photoelectrochemical system by interface manipulation.

(3) Identify improved characterization methods for interfaces and bulk materials in photoelectrochemical systems.

(4) Identify most cost-effective fabrication of photoelectrochemical system interfaces and structures (e.g., use interphase protective layers, buried junctions, catalytic interfaces, or nanostructures).

(5) Improve the synthesis, detoxification, and stability of materials used in the fabrication steps.

10. Organized Molecular Assemblies

The opportunities for technology applications of organized molecular assemblies are plentiful in areas 1 through 6, and 9 above. The most important effort is to focus on using self-assembled monolayers in applied research areas while continuing fundamental feasibility studies. In the applied research areas, the key research issues are to:

(1) Develop thermally and oxidatively stable self-assembled monolayers from organic and inorganic molecules.

(2) Direct applications to technological substrates (e.g., steels, aluminum, copper, ceramics, glass, and photostable polymers).

(3) Control interfacial properties in fuel cells at the gas/liquid/catalyst/membrane interface.

(4) Develop self-regenerating self-assembled monolayers for passivating corrodible surfaces.

(5) Identify (self-regenerating) self-assembled monolayers for friction control.

(6) Prepare low energy optical component surfaces (e.g., mirrors and photovoltaic modules) that are resistant to soiling and biofouling, and are easily cleaned.

(7) Employ self-assembled monolayers as self-cleaning, self-passivating materials in industrial processing steps.

In the areas of fundamental research, the key research issues are to:

- Develop methods for forming in-plane patterns and features in self-assembled monolayers.
- Use self-assembled monolayers with deposited overlayers as a model system to elucidate interactions between organic functional groups and inorganic species.
- Study self-assembled monolayers as model systems for complex phenomena, including but not limited to wetting, adhesion, friction, wear, fouling, soiling, biofouling, corrosion, mass transfer, change transfer, and electron transfer adhesion.
- Use self-assembled monolayers to understand phenomena in condensed-matter science, cooperative behaviors, phase separations, and the influences of defect frequency and nature.
- Develop new types of self-assembled monolayers, focusing on enhanced stabilities and new types of surface-monolayer chemistry.

- Use self-assembled monolayers as nuclear ion centers for three-dimensional processes, e.g., condensation of water, growth of crystals, and attachment of polymers.

- Use self-assembled monolayers as model systems for two-dimensional organization of complex molecules, in relation to molecular materials.

- Develop computational models for self-assembled monolayers and self-assembled monolayer-related phenomena.

11. Other Areas of Impact

In addition to the examples mentioned above, a program in the surface processing technologies will greatly impact the microelectronic, semiconductor, corrosion protection, and catalyst industries. Technologies dealing with ultrathin films, protective and decorative surface coatings, variable conducting masks, and novel bimetallic alloy catalyst systems rely tremendously on the research progress on a surface processing technology. A DOE-supported technology base program will assist U.S. industry substantially in a wide variety of fields and will allow us to maintain and improve our competitive posture in the global marketplace.

III. EPILOGUE

In using surface processing, two potential major technical barriers need to be overcome. These are:

- Securing stable materials that are compatible with each other, i.e., long-term interface stability, without compromising the performance of the systems, materials, and components for specific applications to transportation and utility technologies.

- Developing combinations of materials that meet the criteria for performance, durability, economics, and user acceptance.

A crucial need and timely opportunity exist to use and extend the scientific and engineering knowledge base in surface processing and applied surface sciences to provide solutions to selected priority problems in the transportation and utility technologies. Current components and systems represent approaches taken in the 1980s that have been adequate for their purposes, but need to be enhanced for future needs.

The emphasis of the surface processing research and development program needs to be on formulating, preparing, characterizing, developing, testing and qualifying where applicable, modifying, demonstrating, and understanding advanced systems, materials, and components for specific applications to transportation and utility technologies that will meet lifetime, cost, and performance requirements for the 1990s and beyond.

To ensure future success in the related transportation and utility technologies, surface processing work needs to be initiated as soon as possible and aggressively pursued to reach the confidence level needed for selecting, guaranteeing, and mass-producing future components/systems for long-term use. The research and development need is cross-cutting or interdisciplinary in nature [2] and requires involvement of industry, academia, and federally funded laboratories.

For DOE, a significant cross-cutting applied research program in surface processing technologies will provide several benefits to all conservation and renewable energy technologies, i.e., it will:

- Create a critical mass of researchers and equipment that each Program Office of conservation and renewable energy technologies can draw upon to solve specific end-use problems.
- Provide a multidisciplinary approach, produce strong synergistic effects, and allow various avenues to be explored to solve a specific problem.
- Make available to the emerging renewable energy technology industries in the United States well-equipped facilities with talented experts to assist in solving specific problems and enhancing the competitive position of U.S. industry in the global marketplace.

The need for a critical mass of researchers with multidisciplinary backgrounds, assisted by state-of-the-art instrumentation, is essential to the success of surface processing research and development. Surface characterization and modification technologies encompass techniques typically developed by physicists and chemists; these techniques are being used and improved upon by physicists and chemists, as well as by materials scientists and electrical, chemical, and other engineers. The problems that need solving also cover a wide spectrum of disciplines. The synergistic effect expected from a multidisciplinary approach will make surface processing research and development unique and allow it to meet its goal of providing a genuine technology-based, cross-cutting, research support for all conservation and renewable energy technologies. The ability of surface processing research and development to impact other major DOE efforts makes it very attractive.

For U.S. industry, in general, a world-class leadership in surface processing is an equally strong impetus for the planning of an research and development program. As indicated in the preceding sections, a variety of technologies can benefit from this type of generic research, and advances in surface processing will allow interested industrial concerns to be partners in this effort and to use the knowledge and the equipment.

Although many different assessments will be made about this workshop, positive results can already be stated. Another opportunity has been provided for increased communication among scientists and engineers including those involved with basic and applied problems. Industrial, academic, and federally funded members of the scientific and technological communities have been involved in the planning and have been made aware of the difficulties in setting priorities, even in a focused subset of surface science. Their dedicated effort in establishing the priorities and identifying the most relevant research issues in surface processing for 10 typical areas of applied surface science has resulted in this document. The task now is for all of us to carry out the most important recommendations.

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3. See listing of workshop and panel reports in Appendix A1.

1. COMPOSITIONAL ANALYSES OF SURFACES AND THIN FILMS BY ELECTRON AND ION SPECTROSCOPIES

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ABSTRACT

An overview is given of the current capabilities, advantages, and limitations of the six techniques in common use for compositional analyses of surfaces and thin films: Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), sputtered-neutral mass spectrometry (SNMS), ion-scattering spectroscopy (ISS), and Rutherford backscattering spectroscopy (RBS). Information is also given on efforts to improve these techniques and on the potential of other methods for determining surface compositions during processing.

I. INTRODUCTION

Surface and interface properties are crucial in many different energy and transportation techniques, as is clear from the present workshop. While particular properties such as corrosion- or wear-resistance, reactivity, and electrical properties are needed for specific applications, these depend on the chemical composition at the surfaces or interfaces of interest.

Six techniques are frequently used for determining the composition of the outermost several atomic layers of a material: AES, XPS, SIMS, ISS, SNMS, and RBS. Measurements with the first four of these techniques are generally made in an ultrahigh vacuum (UHV) environment; SNMS can be performed in UHV depending on the method of ionization of the sputtered neutrals. Certain surface processing operations (e.g., heating, film deposition, sputtering) can be carried out in UHV, but often the material of interest has to be transferred to a separate chamber for other types of processing (e.g., interactions with liquids or high-pressure gases). If surface layers of the specimen material are removed by some method (e.g., sputtering), the first five surface-analysis techniques listed above can be used to determine the instantaneous surface composition as a function of time or of distance from the original surface. In this way, the compositions of films with thicknesses up to about 1 µm can be determined together with the local compositions in the vicinity of interfaces. The sixth technique, RBS, is an essentially nondestructive method for measuring near-surface and thin-film compositions in a non-UHV environment.

This report is in two parts. First, the above six techniques are compared and contrasted, based on their capabilities, advantages, and limitations. This section of the report is drawn from a recent book chapter [1]. Second, information is given on future prospects for technique improvements to make them more useful for applications in surface processing. Mention is also made of other techniques that would be useful for these applications.

II. CURRENT STATUS OF MAJOR TECHNIQUES FOR SURFACE ANALYSIS

Information on the major features of the six techniques is summarized in Tables 1-4. Tables 5-10 give information on the relative strengths and weaknesses of the techniques. These summaries are intended only as a semiquantitative guide. The information pertains to commercially available surface analysis systems, in their normal configurations, as opposed to custom-made instruments that optimize a particular parameter. In many cases, trade-offs can and often must be made among the various parameters, e.g., spatial resolution, accuracy and precision of analysis, sensitivity, sample damage, and cost.

A. Principal Features of Techniques

Table 1 gives an overview of the principal features of the techniques. One practical concern in the application of these techniques is the potential for specimen damage by the incident beam. Such damage can take the form of removal of specimen material (e.g., by sputtering or desorption), of changes in specimen composition (e.g., decomposition or polymerization), or of atomic displacements. XPS and RBS are relatively nondestructive, but some materials may be damaged during a prolonged surface analysis. Decomposition is not common in XPS, but prolonged X-ray exposures may damage adsorbates, organic compounds, and some ionic solids [2,3]. AES is essentially nondestructive for metals, alloys, and many semiconductors, but electron beams will rapidly damage organic materials, adsorbates, glasses, and some compounds [3,4]. Electron beam effects are generally proportional to the electron beam dose (primary current density times bombardment time). An electron-beam-induced temperature increase is most detrimental for thin films on substrates with low thermal conductivity. Electron-stimulated desorption is often encountered in studies of ionic compounds. In extreme cases, e.g., for alkali halides, the number of desorbed atoms or molecules per incident electron is greater than one [4]. Charging of insulators is sometimes difficult to avoid and can even lead to induced electromigration. In general, electron beam effects on fragile specimens can be minimized with a low primary electron beam current density, short measurement times, or scanning the incident beam to different regions of the surface.

SIMS, SNMS, and ISS are all intrinsically destructive (i.e., ion bombardment removes specimen material from the exposed surface, and it is not possible to remeasure the composition of a previously sputtered surface). A trade-off must then be made between operating in the "static" mode for true surface analysis and the data acquisition time. The "static" mode requires very low erosion rates [5] and thus low current densities, which also may require optimization between the current density and detection limits (i.e., signal-to-noise ratio). A low incident current density for AES, SIMS, SNMS, and ISS also means that the lateral resolution will be degraded. Ion beams are also used for sputter depth profiling (SDP) to obtain compositional information as a function of depth. Ion bombardment can damage specimens in many ways including, for example, surface roughening, knock-on effects, atomic-scale cascade mixing, preferential sputtering, amorphization and structural changes, decomposition, implantation, chemical state changes, enhanced diffusion, enhanced adsorption, and redeposition [6].

The sampled depth (or information depth) for SIMS and SNMS is listed in Table 1 for the "static" mode; in the dynamic mode (high erosion rates) [5], as often needed for thin-film analysis, the sampled depth may range from 1 to 5 nm or more, depending on the erosion rate, incident beam angle and beam energy used. In RBS, surface monolayers can be studied on single crystals using channeling techniques. The sampled depth depends on the escape depth of the ejected electrons in XPS and AES, on neutralization probabilities in ISS, and on erosion rates in SIMS and SMMS. The American Society for Testing and Materials (ASTM) definition for information depth gives the depth from the exposed surface from which a specified percentage of the detected signal originates. This depth should be distinguished from two other terms, the detection limit (or detectability) and the sensitivity. The detection limit for a particular technique is the minimum quantity of material that can be detected under specified operating conditions and is often expressed as a fraction of an atomic layer; e.g., it is often assumed that the detected material is present as an identifiable phase on a substrate of another material. The sensitivity is the slope of a calibration curve in which the measured signal strength for a given element under specified conditions is plotted versus elemental concentration.

Table 1. Summary of Features of SIMS, SNMS, ISS, RBS, AES, and XPS

Category	SIMS	SNMS	ISS	RBS	AES	XPS
Input "particle"	0.5-20 keV ions	0.5-20 keV ions	0.5-3.0 keV ions	0.5-3.0 MeV ions	2-20 keV electrons	Photons (X-rays)
Damage to sample by input particle	Minimal to extensive depending on beam parameters	Minimal to extensive	Minimal for defocused beam to moderate	Minimal except for organics and polymers	Minimal to extensive for focused e-beam	Minimal (X-radiation)
Output particles	Secondary ions	Secondary neutrals	Input ion	Input ions	Electrons	Electrons
Measured quantity of output particle	Mass/charge of sputtered surface ions	Mass/charge of postionized surface species	Energy of scattered ions after binary collisions	Energy of ion backscattered from elastic collisions	Energy of ejected Auger electrons	Energy of ejected core-level and Auger electrons
Sampled depth	1-2 monolayers ("static")	1-2 monolayers ("static")	Surface monolayer	Many μm into the solid	2-20 monolayers	2-20 monolayers

B. Data Collection

Table 2 summarizes factors important in data collection including vacuum requirements, data acquisition rates, signal-to-noise (S/N) ratio, turnaround time, and depth profiling compatibility. Measurements must be made with a pressure in the vacuum chamber of 10^{-4} Pa or better so that collisions between electrons or ions and residual gas molecules are minimized. Residual gases may react with specimens being analyzed, and pressures of 10^{-7} Pa or lower are generally required to minimize reactions. Another factor is electron-stimulated adsorption, which can lead to oxidation or carburization [4]. Average data acquisition times are given in Table 2, although the actual times may range from seconds to hours, depending on the information desired. The S/N ratio governs the limit of detection; the ranges given should be compared with the detection limits in Table 3.

For SDP, XPS is clearly inferior, because the ion beam etching and surface analysis must be done alternately as a result of the relatively long data acquisition time and the relatively large X-ray beam size, even for current "small-spot" XPS systems. Otherwise, a depth profile is obtained with an inferior depth resolution. However, XPS (as well as AES) can be used nondestructively to obtain depth profiles for shallow depths (≤ 50 Å) by detection of ejected electrons at different takeoff angles. This technique makes use of the variation of electron escape depth with takeoff angle; it is especially powerful when there are electrons with widely different energies and thus escape depths for the same element. In custom-designed RBS systems, near-surface nondestructive SDP may be obtained using channeling and grazing-exit detector techniques. SIMS and AES combined with ion erosion are the two most widely used SDP techniques.

In recent years, the analog instrumentation for recording spectral intensities has been replaced by digital data systems. These systems are extremely powerful for data acquisition and manipulation.

C. Features of the Analytical Methods

Important features of SIMS, SNMS, ISS, RBS, AES, and XPS are summarized in Table 3. Each technique is able to directly identify elements with atomic numbers of 3 and higher. The elements H and He can be detected by SIMS and SNMS, by forward scattering in ISS, or by nuclear reaction analysis (NRA) with RBS equipment. Hydrogen has been detected in some materials by AES and XPS from a detailed analysis of the spectral lineshapes of other elements. The mass-sensitive techniques can detect isotopes, but this capability is limited in ISS and RBS by poor peak resolution for mid- to high-Z elements. SIMS and SNMS have the lowest detection limits, but SIMS suffers from wide sensitivity variations with Z.

None of the ion spectroscopies provides the detailed chemical information obtained with the electron spectroscopies, especially XPS. Small chemical shifts of elemental lines in XPS can be used to identify different chemical states of an element; such identifications are extremely valuable (e.g., in identifying surface reactions or processes). Auger lines also appear in XPS data and typically also show chemical shifts. The difference in XPS and AES peak positions for an element, the so-called Auger parameter, often has a chemical shift. Not only is the latter shift a useful diagnostic, but it may be the easiest to measure reliably on nonconducting specimens. AES, as practiced with electron excitation, has usually been done with analyzers of low energy resolution. Thus, the chemical information (shifts of elemental lines and changes of peak shapes) obtained from the technique has been limited. In some cases, chemical species can be identified by AES data alone, but the supporting data are much less than for XPS. Static SIMS is also very useful, although it can be difficult to extract this information due to the complicating signals from sputtered cluster ions and molecular fragments. Recent experiments using SIMS with high mass resolution have been particularly valuable in identifying organic materials on surfaces.

Table 2. Factors Important for Data Collection in Surface Analysis by SIMS, SNMS, ISS, RBS, AES, and XPS

Factor	SIMS	SNMS	ISS	RBS	AES	XPS
Vacuum (Pa)[*]	10^{-4} to 10^{-8}	10^{-4} to 10^{-8}	10^{-4} to 10^{-8}	$< 10^{-4}$	10^{-4} to 10^{-8}	10^{-4} to 10^{-8}
Acquisition time	Seconds	Seconds	Minutes	Minutes	Seconds	Minutes
Signal/noise ratio	up to 10^{9}	10^{6}	10^{2} to 10^{4}	10 to 10^{3}	10^{2} to 10^{3}	10^{2} to 10^{3}
Turnaround time	Fast[+]	Fast[+]	Fast[+]	Fast	Fast[+]	Fast[+]
SDP[**]	Most natural for SIMS/SNMS because sample erosion is required		Easily done with bombarding beam	Automatically done and non-destructively	Easily done with an auxiliary ion gun	Laboriously done with an auxiliary ion gun
Other depth profiling methods	NA	NA	NA	Yes[++]	Yes[++]	Yes[++]

[*] Although data can be collected at pressures as high as 10^{-2} Pa, contamination of the specimen by the residual gases is a serious concern depending on the reactivity of the surface. Note: 1 Pascal = 7.5×10^{-3} Torr.

[+] Fast with instruments equipped with rapid-sample-introduction or load-lock facility. Turnaround is slow if samples are loaded onto a carousel and a flange has to be rebolted to the vacuum system.

[**] Does not include artifacts in the sample resulting from ion bombardment, which are the same for all analytical techniques except RBS.

[++] See text.

Table 3. Summary of Analytical Features of SIMS, SNMS, ISS, RBS, AES, and XPS

Feature	SIMS	SNMS	ISS	RBS	AES	XPS
Elements not directly detected	None	None	H, He	H, He	H, He	H, He
Detection of H, He	Yes	Yes	$\theta < 19°$ (H)* $< 42°$ (D)	With NRA	Line shapes of other elements in a compound	
Isotopes	Yes	Yes	Low Z	Low Z	No	No
Detection limit (at. fraction)	10^{-6} to 10^{-9}	10^{-6}	10^{-2} to 10^{-4}	10^{-1} to 10^{-4}	10^{-2} to 10^{-3}	10^{-2} to 10^{-3}
Variation of detection limit with Z	10^{4} to 10^{5}	10 to 100	$\sim 10^{2}$ (Li to U)	$\sim 10^{3}$ (Li to U)	~ 20	~ 20
Chemical information and value/usefulness	Yes Some	Yes Some	Yes, but only for eight elements	No NA	Yes Considerable	Yes Outstanding
Other information	Polymers and organics, m/Z to 10,000 and beyond for SIMS; spectra are matrix-dependent, but much less so for SNMS		Shadowing of adsorbate over-layers on single crystals	Surfaces of epitaxial films	Plasmon loss structure, chemical shifts, lineshape changes	Chemical shifts, oxidation states, valence band structure
Information on compounds	Yes	Yes	Rarely	No	Frequently	Yes
Organic samples	Yes	Yes	No	No	Damage likely	Yes
Surface structure	Some	Some	Adsorbates on single-crystal substrates	Epitaxial films	Adsorbates on single-crystal substrates, epitaxial films	
Peak interference^{+}	Rare	Some	None	None^{+}	Occasional	Occasional
Elemental specificity**	Excellent	Very good	Good—low Z; Poor—high Z	Good—low Z; Poor—high Z	Very good	Very good
Lateral (x-y) resolution	0.1 μm	0.2-5 μm	0.1 mm	1 mm	20-100 nm	20-100 μm

Table 3. Summary of Analytical Features of SIMS, SNMS, ISS, RBS, AES, and XPS (Concluded)

Feature	SIMS	SNMS	ISS	RBS	AES	XPS
Lateral imaging and value	Yes Very good	No NA	Yes Poor	No NA	Yes Outstanding	Yes Good
Charging problems	Yes	Yes	Yes	No	Yes	Yes
Quantification sensitivity factors	Vary by up to 10^5 in different matrices	Yes for given instrument	Yes, but small data base	Complete	Yes	Yes
Standard deviation (for repeated measurements)	5%-100%	5%-10%	5%	2%	1%-5%	1%

* θ is ion scattering angle.

⁺ Extent to which there may be accidental overlaps of spectral peaks due to two or more elements. For RBS, signals at energies corresponding to certain elements can overlap signals due to other elements at different depths.

** Extent to which two or more elements can be distinguished due to finite instrumental resolution.

It is possible now to measure femtomoles of small organic molecules (molecular weight ~ 300) and to obtain structural and molecular weight information for polymers. One can detect small molecules on polymer surfaces or one polymer on another.

Each technique can provide different additional information about a specimen material. For example, information about electronic structure can be obtained from XPS and AES. Structural information for adsorbed molecules or thin epitaxial films can be obtained from the angular distributions of photoelectrons or Auger electrons. The energy-loss structures in the vicinity of the elastic peak due to excitations of valence and core electrons in electron-excited AES can be analyzed to give electronic and local structural information.

Peak interferences can occur in AES and XPS but are usually only an annoyance (e.g., for compounds with a large number of elements). An advantage of XPS is that accidental overlaps of photoelectron and Auger peaks can be identified and overcome by changing the X-ray energy. High-resolution mass spectrometers can separate peaks with nearly identical mass/charge ratios in SIMS, but the broader peaks obtained with many SNMS instruments can lead to some ambiguity in peak identification for more complex specimens. Both ISS and RBS are severely limited in elemental identification when analyzing samples with several high-Z elements.

The highest lateral resolution is attained at present with AES. The indicated AES resolution in Table 3 is achieved, however, only with robust specimens that are not damaged by the high bombarding current density. In addition, only major constituents of the surface region (with atomic concentrations ~ 10%) can be detected with such lateral resolutions [5]. Very good lateral resolution, about 0.1 μm, is achieved in SIMS, although then with relatively high erosion rates of the surface (i.e., "dynamic" SIMS). Time-of-flight SIMS, however, enables greater efficiency in mass analysis compared to dispersive analyzers, and correspondingly smaller erosion rates can be employed for a given lateral resolution. Considerable effort has been made in recent years to improve the spatial resolution of XPS. Although the lateral resolution with XPS is now poorer than that in AES or SIMS, it should be remembered that X-ray excitation is generally much less damaging to a surface than electron or ion bombardment and that the chemical state information in XPS can be very useful.

High spatial resolution is clearly important if the specimen is inhomogeneous. Practical materials can have different types of inhomogeneities as well as finite roughness and perhaps complex morphologies. High spatial resolution is then desirable for establishing the existence of multiple surface phases and, if so, their spatial arrangement. Even if a detailed compositional map of the surface is not needed, multiple high-resolution analyses can be required at different surface regions to ensure that representative and statistically adequate information is acquired [5].

Although most surface analyses performed are qualitative, there is increasing interest in quantitative measurements, particularly with the availability of data systems for processing acquired spectra. Physical models have been developed for relating observed spectral intensities to elemental concentrations, but only in the case of RBS is the model well established and the needed parameters readily available [5]. Most quantitative analyses with AES and XPS are made with the use of elemental sensitivity factors, but matrix effects, mainly the variation of attenuation lengths for Auger electrons or photoelectrons from a given element from one matrix to another, can cause errors of about 20%-50% [7]. Matrix effects in SIMS can be substantial (up to a factor of 10^5), but useful quantitative analyses can be obtained with appropriate standards [5,8]. Matrix effects in SNMS are much reduced compared to SIMS, but more studies are needed of matrix effects on the energy and angular distributions of sputtered neutrals. In ISS, variations of elemental signals in different matrices of up to an order of magnitude can occur; these variations are due in large part to changing ion neutralization probabilities. Standard materials, with compositions approximating those of the specimens to be analyzed, provide a relatively straightforward means of minimizing matrix and instrumental uncertainties. It is not generally easy to prepare standards with similar properties (distribution of surface phases, roughness, etc.) to the specimens, but ion implantation has been shown to be a useful method for generating a reference signal in SIMS [8]. The high surface sensitivity of ISS is such that care has to be exercised in avoiding surface impurities such as adsorbed gases.

D. Versatility, Ease of Use, and Supporting Data

Table 4 shows qualitative comparisons of selected features of the analytical techniques. The symbols give a rough guide to the various features to supplement the information given in Tables 1-3.

Successful use of a particular technique depends on the availability of needed reference data. Table 4 gives an indication of the extent to which needed data are available [8-11].

Information is also given in Table 4 on the relative use of the six techniques in recent years and the effective takeoff year, that is, the year in which publications started to grow following the introduction of commercial equipment [9].

E. Summary of Advantages and Limitations

Specific advantages and limitations of SIMS, SNMS, ISS, RBS, AES, and XPS are summarized in Tables 5-10. These tables, together with the information in Tables 1-4, give an overview of these techniques for surface analysis. More details concerning instrumental capabilities can be found in other review articles [5,9,12-19]. Other reviews [20-22] give information on the applications of the surface analysis techniques to many types of materials problems.

Table 4. Comparisons of Selected Features of SIMS, SNMS, ISS, RBS, AES, and XPS. The number of plus symbols indicates a value from poor (+) to very good (+++++).

Feature	SIMS	SNMS	ISS	RBS	AES	XPS
Versatility	++++	+++	+++	+++	++++	++++
Ease of use	+++ (dynamic) + (static)	+++	++++	++++	++++	+++++
Thin-film SDP	+++++	+++++	+++	+++++	+++++	++
Simplicity of data interpretation	++++	+++++	+++++	+++++	+++	++++
Accuracy of quantitative analysis	+	++++	++	+++++	++++	++++
Availability of reference data	++++ (dynamic) + (static)	+	+++	+++	+++++	+++++
Approximate percentage of use 1985-1990	24	2	3	5	33	33
Effective takeoff year	1973	1984	1974	1967	1969	1969

Table 5. Major Advantages and Limitations of SIMS for Surface Analysis and Sputter Depth Profiling (SDP)

Advantages

- is sensitive to outermost 1-2 monolayers (static mode)
- can detect 10 ppm or less
- can acquire SDP data as surface is eroded during analysis
- can detect isotopes
- can detect H and D
- can acquire data rapidly
- has lateral imaging capability

Limitations

- requires destruction of sample for the analysis
- is quantitative with difficulty, at best
- has varying elemental sensitivity
- has complex spectra
- may cause chemical state changes from ion bombardment

Table 6. Major Advantages and Limitations of SNMS for Surface Analysis and Sputter Depth Profiling

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Advantages

- is sensitive to outermost 1-2 monolayers (static mode)
- can detect 10 ppm or less
- can acquire SDP data as surface is eroded during analysis
- can detect isotopes
- can detect H and D
- is quantitative with modest use of standards (a major improvement over SIMS)
- can acquire data rapidly

Limitations

- requires sample destruction
- has poor lateral resolution
- may cause chemical state changes from ion bombardment

Table 7. Major Advantages and Limitations of ISS for Surface Analysis and Sputter Depth Profiling

Advantages

- is sensitive to first monolayer
- can detect 10^{-2} to 10^{-4} monolayer
- is good for SDP
- is useful for studying ordered surfaces and adsorbates
- is excellent for segregation and/or altered layer studies
- can detect isotopes (^{16}O-^{18}O, ^{14}N-^{15}N, ^{32}S-^{34}S)
- has simple spectra
- provides chemical information for a few surface compounds
- can be quantitative with standards

Limitations

- has poor lateral resolution
- has poor specificity for high-Z elements*
- is destructive although erosion rate can be less than a monolayer/h
- requires better understanding of ion neutralization
- generally provides no chemical information

* For example, with incident ^4He ions and a scattering angle of 138°, the following pairs of elements can be resolved: Na and Mg, Fe and Cu, and Ba and Ta. Better resolution can be obtained for high-Z elements with incident neon or argon ions.

Table 8. Major Advantages and Limitations of RBS for Surface Analysis and Sputter Depth Profiling

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Advantages

- is quantitative without standards
- can detect atomic fractions of 10^{-1} to 10^{-4} depending on Z
- directly measures depth distributions below the surface without sample destruction
- has rapid data acquisition
- is especially sensitive to high-Z elements
- has modest vacuum requirements except for surface studies
- can be customized to study surface monolayers
- can resolve some low-Z isotopes
- can be combined with nuclear reaction analysis for detection of H, He, and other low-Z elements

Limitations

- has poor lateral resolution
- provides no chemical information
- cannot resolve different elements of the same mass
- is limited for detecting low-Z elements
- requires lateral uniformity of sample
- is limited by overlapping signals due to mass and depth
- is limited to specimens with only a few elements

Table 9. Major Advantages and Limitations of AES for Surface Analysis and Sputter Depth Profiling

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Advantages

- is sensitive to 2-20 monolayers
- can detect ca. 10^{-3} atomic fraction
- is outstanding for SDP
- has a sensitivity range within a factor of 20
- has superb lateral resolution
- gives chemical information for some elements
- can acquire data rapidly

Limitations

- may alter surface composition
- may have severe charging problems for nonconducting specimens
- is of limited value for organic materials
- has a slow rate of element mapping

Table 10. Major Advantages and Limitations of XPS for Surface Analysis and Sputter Depth Profiling

Advantages

- is sensitive to 2-20 monolayers
- can detect 10^{-3} atomic fraction
- is especially useful for chemical shifts from the same element in different compounds
- is least destructive of all techniques
- has a sensitivity range within a factor of 20
- has minimal sample charging

Limitations

- has moderate lateral resolution
- is slower for SDP than other methods

III. FUTURE PROSPECTS

While AES, XPS, SIMS, SNMS, ISS, and RBS have proven to be very useful for solving a wide range of materials and surface processing problems, they each have significant limitations, as summarized in Tables 5-10. A brief summary will now be given of recent efforts to overcome or minimize some of the major limitations of these techniques. Information will also be given on other techniques for surface and thin-film analyses in surface processing applications.

A. Recent Improvements to Current Surface Analysis Techniques

1. Spatial Resolution

Strong efforts are being made to improve the lateral resolution of AES, XPS, and SIMS, in particular. For AES, field-emission cathodes and parallel-detection schemes are being used to improve lateral resolution without reducing data-acquisition times. Different types of X-ray focusing optics are being developed to utilize the very intense photon beams at new synchrotron light sources for XPS with lateral resolutions in the 0.1-1.0 μm range. Liquid-metal ion sources and time-of-flight mass analyzers have recently led to improved lateral resolution for SIMS. Depth resolution in sputter-depth profiling can be optimized by careful attention to the factors that can degrade measured profiles [6]. Measurements of Auger-electron or X-ray photoelectron intensities as a function of takeoff angle can be analyzed to give depth profiles for shallow depths (up to about three times the relevant electron attenuation length) nondestructively, although statistical fluctuations in the data can lead to nonunique solutions, and angular anisotropies due to specimen crystallinity may cause additional complications [23].

2. Quantitative Analyses

Despite the conceptual simplicity of the surface analysis techniques, there are many sources of systematic errors and artifacts [24]. Seah, however, has reported calibration schemes for the energy and intensity scales of AES and XPS instruments [25]. Improved techniques, based on a valid physical model of electron transport, have been developed for background correction in XPS, and these should also be applicable to AES [26]. The same techniques have also been used to obtain depth distributions (again for shallow depths) nondestructively [27]. A major problem in quantitative AES and XPS concerns the so-called matrix correction for elemental sensitivity factors [7]; recent calculations of electron inelastic mean free paths (IMFPs) have led to the development of a predictive IMFP formula for 50-2000 eV electrons that can be applied to various materials [28]. Prutton and coworkers [29] have developed an advanced scanning Auger microscope and improved algorithms for the correction of topography effects, beam-current changes, and backscattering effects. Both resonant and nonresonant laser postionization schemes are being developed for quantitative analyses by SNMS [30].

3. Reference Data

Efficient use of any characterization technique on a wide range of materials requires the availability and accessibility of needed reference data. For AES, XPS, and SIMS, handbooks have been published with spectral data needed for most solid elements and for a limited number of compounds. NIST has recently announced the availability of an XPS data base containing over 13,000 entries for core-electron binding energies, doublet splittings, and kinetic energies of X-ray-excited Auger electrons that appear in typical XPS measurements (with Aℓ or Mg characteristic X-rays) [11]. The American Vacuum Society is in the process of creating a data base of AES and XPS spectra that will be published in a new journal, Surface Science Spectra, beginning in 1992. An evaluated set of ion sputtering yield data for elemental solids bombarded by ions and with energies relevant for SDP and SIMS will be published soon [31].

B. Other Techniques

One of the limitations of AES and, to a lesser extent, XPS is the limited amount of chemical information they provide. Other techniques such as high-resolution electron energy-loss spectroscopy (HREELS), infrared spectroscopy, or Raman spectroscopy, can give useful supplemental information, particularly for molecules adsorbed on surfaces [32].

A major limitation of AES, XPS, SIMS, and ISS is that they are generally restricted to UHV environments; in one method of SNMS, the specimen is exposed to an argon plasma. Some scientists, nevertheless, have used efficient differential pumping arrangements to analyze solids or liquids with XPS in local environments where the pressure was in the vicinity of 10^{-2} Pa. It also might be possible to perform XPS at higher gas pressures with synchrotron sources of X-rays and in places where the gas atoms or molecules near the specimen act as a "converter" [33]. Total-reflection X-ray fluorescence offers a more general means of analysis at atmospheric or higher pressures but not, however, with the surface sensitivity of the techniques considered here.

Electron microscopy is a highly developed technique for materials characterization [34-37]. Modern scanning transmission electron microscopes equipped with electron energy-loss spectrometers can be used to probe chemical changes in the vicinity of solid-solid interfaces with a lateral resolution of about 0.4 nm. Atom-probe field ion microscopy can also be used to characterize solid-solid interfaces and the composition of small grains with comparable spatial resolution [38]. For both forms of microscopy, special specimen preparation techniques are needed.

High resolution scanning electron microscopes have been developed to study surfaces and thin-film nucleation and growth phenomena in a UHV environment [39]. Elemental analysis with submonolayer sensitivity has been attained by measuring characteristic X-ray emission at near-grazing takeoff angles [40]. Recent efforts to improve the spatial resolution in electron microscopy and various forms of electron spectroscopy have been summarized in the report of a recent workshop [41].

Scanning tunneling microscopy and atomic force microscopy can be used to obtain topographic information and other surface properties. These techniques cannot be used, in general, for compositional analyses of "unknown" surfaces.

IV. SUMMARY

AES, XPS, SIMS, SNMS, ISS, and RBS are powerful techniques for the analysis of surfaces and thin films. A careful selection of one or more techniques is needed to ensure that a problem can be solved, given the capabilities and limitations of each method. Complementary techniques may often be needed, however, to provide more specific chemical information, higher spatial resolution, or the ability to monitor chemical changes at solid-fluid interfaces. The report of an earlier workshop analyzes different approaches for characterizing the microstructure and microchemistry of interfaces [42].

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2. CHARACTERIZATION OF SURFACES: CURRENT STATUS OF SURFACE STRUCTURE DETERMINATION

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I. INTRODUCTION

The first purpose of this paper is to provide a brief overview of the current status of the determination of the atomic structure of solid surfaces. We organize this survey by classifying surfaces by type (clean versus overlayer geometries; metallic, semiconducting, and insulating substrates) and presenting an aggregate view of the results for each type. We further consider only surfaces whose atomic geometry is known quantitatively, which usually restricts our attention to epitaxial overlayer structures. Finally, we cite the review literature almost exclusively, using original sources primarily for illustrative examples. Coverage is restricted to solid-gas (i.e., vacuum) surfaces, as opposed to solid-solid or solid liquid interfaces.

The second purpose of this paper is to indicate some of the current key issues in surface structure prediction and measurement. For example, it has been proposed that the cleavage surfaces of both zincblende [1] and wurtzite [2] crystals exhibit essentially universal structures if all distances are measured in units of the bulk lattice constant. Moreover, these nearly universal relaxed surface structures revert to their bulk form on the adsorption of Sb or Bi [3,4]. Indeed, the issue of adsorption-induced reconstructions is a topic of great interest in studies of surface chemical reactions, including catalysis [5]. In the case of compound semiconductors, a good example is Al on GaAs(110), which forms epitaxial AlAs "layer by layer" on annealing [3]. Important issues concerning these reactions involve their spontaneity (as opposed to activation), their dependence on the initial surface structure, and the extent to which they disrupt the initial surface structure.

The paper is organized into two context-setting sections on theoretical concepts and experimental methods in the prediction and measurement, respectively, of surface structures. These are followed by synopses of available results on clean and adsorbate-covered surfaces. The references are designed to afford an entre into the pertinent literature.

II. CONCEPTS IN THE THEORY OF SURFACE STRUCTURE

Metallic surface structures are determined primarily by the self-consistent electrostatic response of surface ion cores to the metallic electrons spilling out into the vacuum. Recent reviews have been given by Hamann [6] and Inglesfield [7, 8]. For close-packed surfaces (e.g., fcc <111>), these ion-core relaxations are oscillatory but small. They can, however, become quite significant for more open surfaces (e.g., fcc <210>). An important general concept is the recognition that the electron density deviates from its bulk value only for a few angstroms into the bulk, so the ion-core relaxations are confined to this depth (which can be as many as 10 or so atomic layers on the more open faces). Exemplary systems and models are discussed by Chen et al. [9], by Sokolov et al. [10], and by Marcus and Jona [11].

For transition metals, additional phenomena may occur. For example, at low temperatures (T < 220-250 K), the (100) surfaces of both W and Mo reconstruct to form lower symmetry structures that are one-dimensional chains of atoms on the bcc (100) substrate [7]. This phenomenon has been attributed to both collective effects (charge density wave formation) [12] and to the formation of d-electron chemical bonds [7,13]. If the latter is the case, then these surfaces are examples of surface rehybridization: a phenomenon that is ubiquitous in the relaxation and reconstruction of semiconductor surfaces. W(100) and Mo(100) also are among the first systems in which adsorbate-induced (in this case hydrogen) reconstruction of a clean metal surface was observed [14], and they remain [15] a topic of current interest for this reason. Fcc transition metal surfaces also exhibit reconstruction, i.e., a surface structure that exhibits lower symmetry parallel to the surface than the bulk substrate. Well-known examples include the (100) and (110) surfaces of Ir, Pt, and Au. At high temperatures, these surfaces may revert back to (1x1) structures via phase transitions that are believed to be order-disorder transitions. A review of the theory of reconstructions and relaxations at clean metal surfaces has been given by Inglesfield [7].

Semiconductor surface reconstructions and relaxations are most easily interpreted in terms of the rehybridization of the valence electron charge of surface species to minimize the "dangling bond" charge density. In the case of elemental semiconductors and the polar surfaces of compound semiconductors, this rehybridization drives massive structural changes in which chains [e.g., Si(111)-(2x1)], dimers [e.g., Si(100)-(2x1)], trimers [e.g., GaAs(-1-1-1)-(2x2)] and other more complex surface species [e.g., Si(111)-(7x7)] are formed. In the case of the nonpolar surfaces of tetrahedrally-coordinated compound semiconductors, the rehybridization results in large atomic displacements that are enabled by surface topologies that admit bond-length-conserving surface relaxations. Recent reviews of both experimental structures and their theoretical interpretation have been given by Duke [3] and Schluter [16] for compound and elemental semiconductors, respectively.

An important concept that has emerged from the study of the atomic geometries of the cleavage faces of tetrahedrally-coordinated compound semiconductors is the notion of surface-structure universality [1-3,17]. This notion consists of an observation and its interpretation. The observation is that when scaled with the bulk lattice constant, the (110) surface structures of all zincblende structure III-V and II-VI compound semiconductors are identical to within experimental error. The interpretation is that this result is due to a universal mechanism of rehybridization associated with the lowering of an anion-derived surface state from mid-gap to the top of the valence band by virtue of a nearly bond-length-conserving rotation of the uppermost chain of surface atoms to a tilt angle of $\omega = 29° \pm 3°$ to the unrelaxed surface. This rotation, and its accompanying small contractions in the back and surface bond lengths, leads to the redistribution of the surface state charge from the "dangling bond" on the unrelaxed surface to the back and surface bonds in the relaxed surface. A similar universality of the surface structures and relaxation mechanisms was predicted for the (10-10) and (11-20) cleavage surfaces of wurtzite structure compound semiconductors [2,17] which current experiments are validating [18]. A consequence of this concept is that in analogy to bulk crystal structures [19], the equilibrium surface structures of semiconductors exhibiting homologous types of bonding will all be identical to within scale factors depending only on the bulk crystal lattice constants. Similar concepts should apply to metals but have not yet been formulated for this class of surfaces.

The transition from semiconductors characterized by predominately covalent bonding to insulators characterized by predominately ionic bonding is often defined in terms of correlations of ionicity with bulk crystal structure [19]. In this view, "covalent" bonding results in tetrahedrally-coordinated structures (e.g., zincblende, wurtzite), whereas "ionic" bonding results in six-fold coordinated structures (e.g., rock salt). From the perspective of surface structure, this is an important distinction because the topologies of the nonplanar cleavage (or fracture) surfaces are quite different in the two types of structures. The cleavage surfaces of tetrahedrally-coordinated compound semiconductors admit large bond-length-conserving relaxations in which the cations' local coordination can change from tetrahedral (sp^3) to planar (sp^2). Moreover, these surfaces exhibit large relaxations to approximately planar cation coordination. In contrast, nonpolar surfaces of cubic crystals, e.g., rock salt(100), require large bond-length distortions to alter significantly the surface-atom coordination. Although the surface rehybridization may stabilize a relaxed surface structure, materials with these structures exhibit only small surface relaxations because the energy required to distort the bonds produces a large kinetic barrier to reaching such a structure under reasonable processing conditions. Reviews of these ideas have been given by Duke and LaFemina [20,21].

Some species, like Xenon, adsorb gently and reversibly on clean surfaces ("physical" adsorption) and may even be used to decorate surfaces to determine their topography [22]. Most, however, form bonds with one or more surface atoms ("chemisorption"), thereby inevitably disrupting the clean surface to some extent. In such cases, the surface structures that are formed are usually out of equilibrium because of kinetic barriers to the energetically favored chemical and structural transformations. Indeed, the semiconductor electronics industry is based on the generation of such nonequilibrium structures by cycles of chemical and thermal processing. Therefore, the central concept in the surface structure of overlayer systems is that "what you get depends upon how you got it," i.e., the structure is determined by the process history of the sample.

Within this context, systematic studies of surface reactions have led various authors to propose taxonomies of adsorbate-substrate systems depending on the degree to which the adsorption event disrupts the surface. Somorjai and Van Hove classify systems according to whether they exhibit adsorbate-induced relaxation, reconstruction, or compound formation [5]. Duke distinguishes between reactive chemisorption and epitaxially constrained adsorbate bonding [23]. Avouris and Lyo classify reactions on silicon according to whether they are "site-selective" or "involve extensive atomic rearrangement" [24]. Braicovich, on the other hand, introduces a complex taxonomy of the entire deposition process to describe the many possible outcomes of metal deposition on elemental semiconductors [25], whereas an entirely different taxonomy is used to describe reactive etching processes [26]. Thus, even a cursory inspection of the literature reveals that, in contrast to clean surfaces, the establishment of general relations between surface structures and the characteristics of equilibrium chemical bonding is of limited use for overlayer systems due to the intimate dependence of these structures on the process steps used to prepare them.

III. METHODS OF QUANTITATIVE SURFACE STRUCTURE DETERMINATION

Our purpose in this section is to provide a brief indication of how the surface structures discussed in subsequent sections were determined. It is useful to distinguish between methods used on surfaces exhibiting long-range two-dimensional periodic order parallel to the surface, those employed to obtain the local configuration around a given atomic species, and those used to assess surface topography (i.e., steps, terraces, etc.). Surveys of the various techniques may be found in the literature [27] and are given elsewhere in these proceedings. Compilations of surface structures have been published in which the technique used to obtain a given structure is included in its description [27,28]. Our discussion reflects their content and the development of new techniques within the past few years.

For surfaces exhibiting long-range periodic order, the quantitative surface structure determination method of choice is overwhelmingly low energy electron diffraction (LEED) intensity analysis [11,29-33]. In recent years, this method has led to the determination of multilayer metal surface relaxations [5,11,28] and small [e.g., (1x1), (2x1), and (2x2)] semiconductor surface structures [3,16,20,32,33]. The method also has been used to refine large structures, e.g., Si(111)-(7x7) [33]. Historically, the determination of the Si(111)-(7x7) structure was enabled by ultrahigh vacuum high resolution transmission electron diffraction (HRTEM) [34] and refined by LEED and glancing angle X-ray diffraction [35]. The latter recently has become much more common [35]. It is the technique of choice to examine displacements parallel to the surface of large unit cell semiconductor structures [35] and has been applied successfully in other cases as well, such as W(100) [36]. Finally, during the past 2 years, low energy positron diffraction (LEPD) intensity analysis has been shown to be a competitor to LEED for the determination of semiconductor surface structures [37].

Ion beam techniques also have found extensive use in quantitative surface crystallography, especially for small unit cell structures [38]. These techniques are sensitive to displacements parallel to the surface and hence afford an important complement to LEED or LEPD which, as usually practiced with near normal incidence particles, are sensitive predominately to displacements normal to the surface. Since quantitative analysis of the ion-scattering data is done by Monte-Carlo simulation, the methodology is useful predominately for the a priori determination of simple structures or for discriminating between different models of complex structures. A related technique, shadow-cone-enhanced secondary ion mass spectrometry, has been proposed recently but its application to GaAs(110) failed to recover the well-known structure of this surface [39].

In addition to their use for the determination of the atomic geometries of ordered regions of surfaces, electron diffraction techniques can be used to examine the topography (i.e., the occurrence of steps, islands, terraces, etc.) of imperfect surfaces. A direct way to do this is to refocus the diffracted LEED beams (in practice, the specular beam) to obtain an image of the surface [40]. This technique, called low energy electron microscopy (LEEM), has been used to study steps on Si surfaces and overlayer islands on both Si and Mo [40]. Alternatively, the shape of the diffracted beams as a function of exit angle in the neighborhood of the diffraction direction can be measured and analyzed to obtain similar information. Pioneered by Henzler [41] and Lagally [42], this methodology has been reviewed recently by Wollschläger et al. [43]. Individual atomic defects also can be imaged directly by field ion microscopy for those materials that can be formed into sufficiently stable tips [44]. This technique is particularly useful for studying adsorbate diffusion and interactions between adsorbates, especially on transition metals [44].

It is not necessary for a surface to exhibit long-range periodic order to be able to determine features of its atomic geometry, as already noted above for field-ion microscopy. Historically, the analysis of fine structure in various core-level excitation and filling processes, called Surface Extended X-ray Absorption Fine Structure (SEXAFS) in the case of the detection of Auger electrons associated with the filling of an empty core state near the surface, has been used to determine the local coordination of the excited species [45-47]. Similar local diffraction phenomena occur in photoemission and in the Auger process itself, leading to the development of X-ray photoelectron and Auger electron forward scattering as techniques for assessing local surface structure and its application to metal and semiconductor alloy systems [48]. As widespread working tools for local surface structure examination, these techniques have been eclipsed, however, by the development of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) [24,49,50]. Although of limited use for the precision determination of atomic structural parameters [50,51], the vivid images illustrating the nature of the local surface atomic geometry coupled with the ability to determine the local surface electronic structure has rendered STM the leading new tool for the assessment of the qualitative features of local surface structures on conducting substrates (i.e., metals and semiconductors). STM results have not yet penetrated the surface structure tabulations [27,28], but they have exerted a major impact on the qualitative understanding of reconstructed metal and semiconductor surfaces (e.g., Si(111)-(7x7) [16,49,50]) as well as a variety of adsorbate systems [24,51].

IV. CLEAN SURFACES

This section is devoted to an overview of the current status of knowledge about the atomic geometries of clean surfaces. These structures are dynamic, although this fact is not commonly emphasized. Surface defects in the forms of terraces, steps, and kinks are constantly forming and reforming, leading to surface roughening and even melting at temperatures approaching the bulk melting temperature [52]. The topic of phase transitions at surfaces, i.e., roughening, melting, and wetting, has enjoyed a resurgence in interest during recent years, as described, e.g., in a comprehensive overview by Dash [53]. Such phenomena have been studied by He atom scattering [52], ion-beam scattering [38], glancing-angle X-ray diffraction [35], and LEED angular profiles [43], especially for the high-index ("vicinal") surfaces of Ni and Cu [52], and for Pb(110) surfaces [53]. In the case of reduced-symmetry surface structures ("reconstruction"), order-disorder transitions may occur prior to melting [7,36]. Our ensuing discussion is focused, however, on the low-temperature atomic geometries in the absence of defects, i.e., the surface analogs of the perfectly periodic crystal structures of bulk solids.

A. Metals

The atomic geometries of the surfaces of metals have been determined primarily by LEED [27,28,54] and ion scattering [38,55]. Tables comparing the results of the two methods (mostly for fcc transition metals) have appeared in several reviews [38,55]. For the close-packed faces, i.e., fcc(111), bcc(110), and hcp(0001), relaxations from the truncated bulk structure are small, typically less than 2% [7]: a result that characterizes transition as well as s-p bonded metals. These relaxations increase as the surfaces become more open, driven by the response of the surface ion cores to the smoothed electron density at the surface [7]. The relaxations are oscillatory in nature (contractions of the top layer spacing, expansions of the second layer, etc.), becoming smaller, more or less exponentially, with increasing depth into the crystal. Alloy geometries are more complicated, with puckering between the various components of the alloy occurring in surface and near-surface layers containing multiple components of the alloy [9,55]. Relaxations parallel as well as normal to the surface occur for the more open surfaces [11]. The magnitude of the relaxations decays to less than a percent within a few angstroms of the surface, independent of the crystallographic orientation of the surface [11]. Diagrams of most of these structures may be found in MacLaren et al. [28]. An updated version of the structural tables in References 27 and 28 has been given very recently by Van Hove et al. [56].

Certain transition metal surfaces exhibit reconstruction as well as relaxation. Highly studied systems include the (100) and (110) surfaces of fcc Ir, Pt, and Au [7,38], as well as the (100) surfaces of bcc W and Mo [7,36]. The latter consist of zig-zag chains of W (or Mo) atoms bonded to a slightly relaxed substrate. The top-layer chains are thought to be caused by d-electron bonding of the surface species, associated with the splitting of a partially-filled band of surface states into a fully occupied bonding and an empty antibonding band [7,13]. The nature of the phase transition to the (1x1) high-temperature phase has been the subject of extensive investigation and debate [7]. Recent glancing-angle X-ray studies favor an order-disorder (rather than displacive [7]) transition [36], whereas He atom scattering measurements of the surface vibrational spectra favor a soft-phonon displacive mechanism [57]. The situation with the reconstructed fcc metals is even less settled. LEED, ion-scattering, glancing-angle X-ray diffraction, and STM have been applied to these surfaces, with results that are not always fully consistent [38]. The consensus seems to be that variants of the missing row model describe the fcc(110)-(2x1) reconstruction [7,38], whereas the fcc(100) reconstructions are generated by hexagonal close-packed top layers slightly distorted to achieve epitaxy on the (100) substrate [7]. The nature of the issues that arise in the determination and interpretation of the fcc reconstructed geometries is well illustrated by the account given by Van der Veen [38] of the analysis of the (2x1) structures of the (110) surfaces of Au, Ir, and Pt.

B. Semiconductors

The determination of the atomic geometry of the Si(111)-(7x7) has been the benchmark semiconductor surface structure problem for three decades. Virtually every surface structure analytical method, i.e., LEED [33], ion scattering [38], glancing-angle X-ray diffraction [35], STM [49,50], ultrahigh vacuum (UHV) HRTEM [34], as well as others have been applied to this problem as reviewed, e.g., by Schluter [16]. The key breakthrough was an analysis of HRTEM Patterson maps by Takayanagi et al. [58] to propose a dimer-adatom-stacking fault (DAS) model, a refinement of which is the currently "accepted" structure [16, 35, 38]. This is a three-distorted-layer model on top of a bulk unit cell one half of which is separated from the other half by a surface stacking fault. Useful schematic diagrams and STM images may be found in the reviews by Schluter [16] and Golovchenko [49]. Using atom-resolved tunneling spectroscopy (ARTS), the electronic structure associated with the various inequivalent surface sites has been measured explicitly [24]. There are 200 atoms per unit cell in the top three layers plus the first faulted substrate layer. In the LEED analysis, C_{3v} symmetry was assumed, leaving 49 independent atomic positions to be determined [33]. The fact that a consensus has been reached on at least the approximate positions of these atoms [34] is a measure of the complexity of the surface structures that can be determined with modern surface analysis techniques and enough dedicated effort.

Two other Si surface structures, the (111)-(2x1) cleavage structure (the (7x7) structure is obtained by high-temperature annealing) and the (100)-(2x1) structure, have attracted considerable effort over the years. Histories of the structure determinations of both structures have been given by Schluter [16], and a synopsis of a more recent STM analysis of the Si(111)-(2x1) structure is contained in a review by Feenstra [59]. For Si(111)-(2x1), the consensus surface structure is two layers of "pi-bonded chains" on a relaxed (111) substrate as illustrated in Fig. S69 of MacLaren et al. [28]. For Si(100)-(2x1), it is asymmetric (i.e., tilted) dimers as illustrated in Fig. S68 of MacLaren et al. [28]. STM images have led to questions about the tilting of the Si(100)-(2x1) dimers, a revealing discussion of which may be found in the comments following a paper by Demuth et al. [60] at the 1987 Solvay Conference.

Turning to compound semiconductors, the (110) cleavage surface structures have been determined by LEED for all known zincblende structure III-V and II-VI materials [3]. Moreover, the LEED results have been verified repeatedly by other techniques, especially ion scattering [38]. GaAs(110) was the first semiconductor surface structure to be determined quantitatively [61] and remains the benchmark. A history of its determination by essentially all of the various surface structure analysis techniques is given by Duke [3]. The resulting structure, an approximately bond-length-conserving rotation of the top-layer GaAs zig-zag chains, is shown in Fig. S61 of MacLaren et al. [28]. Tables of references may be found in Van Hove et al. [56]. The importance of these structures resides in their universality for all III-V and II-VI materials. The top-layer chains are twisted by 29°±3° for all materials studied to date, and surface bond lengths are approximately conserved, within experimental uncertainty, although some surface bond compression is suggested [3]. This universality prompted a search for its cause: the lowering of the anion-derived filled surface state band on rotation [2,3]. This lowering depends primarily on the topology of the (110) surface, rather than on the detailed surface electronic structure, thereby establishing a link between surface topology and the character of the surface relaxations.

The current frontiers in this area are analyses of structures for polar surfaces (e.g., those used in molecular beam epitaxy) [3,35], for germanium surfaces [16,35], and for the cleavage surfaces of wurtzite-structure compound semiconductors [17,18]. Accounts and diagrams of most of the quantitative structure analysis are given in the compilations cited previously [3,16,28].

C. Insulators

Relatively little work has been done recently on the surface structures of compound semiconductors that are not tetrahedrally coordinated. Early work on cubic oxides and layered compounds is reviewed by Kahn [32]. Surface structure predictions are being made for other classes of semiconducting and insulating oxides (e.g., cubic, rutile, cristobalite, and tridymite cleavage faces [21]), which reveal system dependencies of the low energy structures on surface topology. These predictions and the concepts on which they are based remain to be tested. Surface phonon spectra [57] and LEPD intensities [37] have been measured for the (100) faces of several alkali halides, but no quantitative analysis of the atomic geometries have been given. LEPD intensities also have been reported for the (111) surfaces of solid rare gases (i.e., Ne, Kr, Ar, and Xe) [37], so quantitative surface structure analyses of these insulators certainly are possible, although not yet attempted. Ordered epitaxial oxides have been reported to be grown at Ni [38] and Si [62] interfaces, but they are not yet well characterized structurally. The deposition of inorganic fluorides on semiconductor substrates is currently a popular topic [66], but no quantitative studies of the vacuum surfaces have been reported.

V. OVERLAYERS

As noted in the introductory sections, the literature on the surface structural chemistry of ordered adsorbed overlayer systems is extensive, complex, and difficult to classify due to the process dependence of the structures. Major reviews, in order of appearance, include those of Somorjai and Van Hove in 1979 [27], MacLaren et al. in 1987 [28], Somorjai and Van Hove in 1989 [5], and Van Hove et al. [56] in 1989. All four of these reviews emanate from the same group of authors and hence exhibit a considerable degree of overlapping. These authors characterize the resulting structures by the extent of the impact of the adsorption on the initial surface structure, with the resulting taxonomy of adsorption-induced relaxation, reconstruction, and macroscopic reshaping [5]. The tabular material in these reviews is extensive, encompassing several hundred surface structures.

Overlayer systems exhibit two major new features relative to clean surfaces that influence the nature of the literature. First and foremost, they are inherently nonequilibrium systems whose analysis is an integral part of studies of commercially important processes in the chemical and electronic industries. Thus, one finds a focus on systems of interest in catalysis [5,63], semiconductor processing for microelectronics [23-26], and molecular beam epitaxy [64-66]. Second, since the adsorbates differ chemically from the substrate, a different set of structural techniques play a major role. The workhorses of LEED [3,5,27,28,54,56], ion scattering [38], glancing-angle X-ray diffraction [35], and STM [24,50,51] are supplemented with vibrational spectroscopy [6,67,68] (especially for adsorbed H [69]), core-level structural spectroscopies [45-48], and structural analyses based on induced desorption phenomena [44,63,70]. Therefore the literature contains both process-oriented reviews that deal with surface structure as one small part [26,64-66] and technique-oriented articles dealing with adsorbate selective techniques [22,24,44-48,63,67-70].

Given the scope of the subject matter and the availability of recent tabulations of structures, we proceed by considering two illustrative examples pertinent to semiconductor processing. As an example of adsorption passivating a surface, we consider a monolayer (ML) of Sb for the system GaAs(110)-p(1x1)-Sb(1 ML). This topic has been reviewed regularly [3,32] and is the subject of recent updates [4,71,72]. As an example of reactive adsorption used in semiconductor processing, we consider the formation of silicides on Si, also a topic of current reviews [25,38]. For a discussion of the (hundreds of) other systems, the reader is referred to the surveys cited [3,5,20,27,28,38,46,48,56,68-71].

A. GaAs(110)-p(1x1)-Sb(1 ML)

When GaAs is cleaved to form GaAs(110), we envisage the formation of two "dangling bond" surface states: one on the As and one on the Ga. Both occur in the gap, but since the Ga state lies higher than the As state, the Ga "dangling bond" electron is transferred to the As, which subsequently relaxes into a distorted p^3 geometry simultaneously with the Ga relaxing to an approximately sp^2 geometry, yielding the 29°±3° tilt of the top zig-zag chain of GaAs as described earlier (e.g., Fig. S61 in [28]). The presence of an Sb monolayer permits a chemically saturated surface, however, removing the driving force for the relaxation. The Sb species occupy sites roughly where the last layer of GaAs would have been. Figures may be found in References 3, 4, 5, 28 (Fig. S65), and 32. Each Sb is three-fold coordinated (one substrate and two neighboring surface species) so that its valence of five is saturated. The surface is nearly unrelaxed, with small tilt angles of approximately 3° in the Sb overlayer and 4° in the top layer of the substrate beneath, as would be expected from the saturated valence. The addition of further Sb leads to the formation of weakly adsorbed islands on top of the saturated monolayer.

The importance of this structure and its Bi analogs [4] resides in its illustration of a new type of surface chemical bond [73]. The Sb overlayer consists of p^2 bonded chains whose pi electrons form bonds with the sp^3 orbitals of the substrate. Several other chemically plausible forms of bonding have been proposed [3,32,72], but all have been shown to be incompatible with the LEED [4] and STM [51] data. Confirmation of the proposed binding mechanism comes from comparison of the calculated [72,73] surface states with those measured by angular dependent photoemission [3,71,72]. Therefore the literature on the GaAs(110)-p(1x1)-Sb system illustrates well the intimate interaction between structural spectroscopy (LEED and STM), electronic spectroscopy (STS, photoemission, and inverse photoemission), and theoretical predictions of the geometrical and electronic structure of the surface, which are required to establish with confidence the nature and consequences of a new adsorbate-induced surface structure.

B. Silicide Growth on Si(111)

A class of systems of considerable commercial interest in which certain adsorbates (e.g., Ni, Pd) disrupt the initial surface structure and form compounds (e.g., $NiSi_2$, PdSi, Pd_2Si, Pd_3Si) is that of metals deposited on Si(111) [25]. These systems constitute the scientific foundation for the multilayer metallization technologies used in making interconnects on Si microelectronic circuits. The central puzzle is the identification of the mechanism for the formation of silicides at the Si(111) surface at temperatures below those required for the growth of bulk silicides. In addition, some of these systems, e.g., Si(111)-Pd_2Si(0001) and Si(111)-$NiSi_2$(111) constitute good examples of the epitaxial growth of metals (the silicides) on semiconductors (Si) of interest as model interfaces for the examination of the electrical properties of metal-semiconductor contacts [25,38].

Structural studies of silicide formation on Si(111) have been reviewed by Van der Veen [38]. The basic idea underlying models of this process is that the formation of metal "clusters" is a crucial intermediate step at room temperature. The energy released in the metal-metal bonding presumably assists in overcoming the kinetic barriers to metal-silicon bond formation, thereby enabling silicide formation. An analogous situation for compound semiconductors is the formation of AlAs surface layers via deposition of Al on GaAs(110): a system studied in great detail a few years earlier [3, 23]. The major tool used to elucidate the process steps is ion-solid scattering with transmission electron microscopy (TEM) and glancing-angle X-ray scattering playing important roles in the determination of the interface geometries for epitaxial silicides on Si(111) once they have been formed [38]. As usual, these determinations occur by successive hypothesis followed by verification or rejection using multiple techniques. An exemplary and extensively studied example is the growth of $NiSi_2$ on Si(111); a good account of this story may be found in Van der Veen's review [38].

VI. Synopsis

Given motivation and financing, surface geometries of rather complex individual structures can be obtained with confidence. Si(111)-(7x7) is the benchmark example [16,33,33-35,38]. In addition, studies of variations of the geometries of a given surface across homologous series of materials have greatly expanded our knowledge of the surface structural chemistry of tetrahedrally-coordinated compound semiconductors [2,3,17,18,20]. Studies of metal surfaces have revealed the occurrence of multilayer relaxations and reconstructions, although their detailed interpretation remains controversial [36,57,74,75]. Adsorbed overlayer structures tend to be even more controversial because of their nonequilibrium character; good examples are Al on GaAs(110) [3,23] and $NiSi_2$ on Si(111) [38]. Moreover, despite claims to the contrary, the role of these structures in complex semiconductor and catalytic processes remains uncertain [25,76]. Thus, the quantitative determination of surfaces has been useful primarily as a testing ground for theoretical models of surface structure and chemistry [3,6-9,12,13,16-21,52,53,56,72, 73]. These ideas can then be extended to technologically useful situations in which the pertinent structures are not directly accessible, as discussed explicitly, e.g., by Ertl [76] for catalysis and by Duke [23,77] for semiconductor processing. Stated alternatively, essentially any interesting inorganic surface structure can definitely be determined, given current surface analysis technologies, for a price. Whether the structure is worth knowing at this price depends almost entirely on the ingenuity and insight of the users of this information for a given purpose: a concept that was articulated and documented nearly a decade ago [77] but which remains as pertinent in 1991 as in 1981.

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3. A SUMMARY OF CRITICAL ISSUES FOR APPLICATION OF IR SPECTROSCOPY TO CHARACTERIZATION OF SURFACE PROCESSING

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I. INTRODUCTION

Although more than several dozen specific techniques are used for the analysis of surfaces and thin films, there always seems to be a need for a new technique. This is because one technique alone rarely solves a given sample analysis problem but rather contributes only pieces of the puzzle. Characterization issues for complex surface and thin-film structures are usually resolved only by the application of combinations of techniques, with each one providing complementary information. By careful evaluation of the limits and errors involved in the interpretation of each piece of data, one can arrive at a self-consistent analysis of important features of the sample of interest. Obviously every technique cannot be applied in every case but rather optimal strategies must be developed to maximize the information for an acceptable level of cost and effort. Neglecting the issue of cost, which is properly dealt with as a local institutional issue, the major issues associated with a given technique become those stemming from information content, interpretative complexity, experimental (instrument and operation) complexity, and sample limitation. In this regard, the purpose of this review is to provide relevant information about infrared spectroscopy (IRS) that will assist in developing characterization for surface and thin film structures in which IRS could be a contributing technique, whether the dominant critical technique or simply a minor confirming one. Because of the much wider applicability of the mid-infrared (IR) wavelength region in chemical analysis, relative to far- and near-IR wavelengths, only mid-IRS will be discussed. In this article, it is assumed that the reader already understands the types of analysis problems for which IRS might be useful and that the reader has a general understanding of a simple IR experiment. In particular, this article is not intended to be a review. Several recent texts treating vibrational assignments [1,2] and instrumentation [3-5] are available for information on this aspect. In Section II, typical characterization goals of a surface/ thin-film analysis are presented. In Section III, a general introduction to IRS is presented. With this as a backdrop, Section IV describes the special case of IRS at surfaces and interfaces with a focus on applications to surface/thin-film analysis. Finally, Section V provides a summary of optimum applications of IRS and directions for future developments of the technique.

II. TYPICAL CHARACTERIZATION GOALS OF A SURFACE/THIN-FILM ANALYSIS

Coverage, thickness, and density are three closely related features necessary for a quantitative assay of a thin film. For film thicknesses of less than a "monolayer," the smallest thickness possible for a uniform film without breaking up the fundamental chemical composition unit of a unit cell or molecule, the amount of film is often given in terms of "coverage," either as the fraction of a monolayer or as a surface density of chemical species per unit surface area. For films with greater than "monolayer" coverages, the thickness is usually used to describe the amount. However, to correctly characterize the amount of material from the thickness, the volume density of the film must be known. Coverage, thickness, and density are all one parameter (average) quantities and can never accurately describe film structure without additional knowledge of density distributions, including such features as roughness and interior voids.

For films of more than one element, it is useful to know both the atomic (or elemental) composition and the chemical composition. The latter includes an assay of the number and types of chemical groups and valence or bonding states associated with the different constituent elements. In addition, for molecular films, other subtleties in structure may be very important, such as conformational sequences and hydrogen bonding interactions. With regard to such molecular fine structure features, and all others as well, it is critical that the analysis be nondestructive.

In many cases, the film structure may exhibit some degree of ordering both with respect to uniform orientations and uniform spacings of chemical bonds or groups. The film thus must be characterized by orientational and translational ordering, which in turn are given properly in terms of the dimensions and symmetry of the simplest structural unit and a correlation length for the persistence of this structure.

The film/substrate interface is characterized both by the nature of the bonding (e.g., physisorption or chemical bonding), the orientations of the bonds, and the relationship between the location of substrate surface sites and film bonding sites (e.g., epitaxial, commensurate, etc.)

The presence of defects and impurities within the film usually presents a severe challenge in quantitative analysis. Defects include voids and boundary regions between ordered domains, and such defects may or may not be correlated with substrate defects. A typical and significant impurity in many organic films on oxide substrates is water bound in the interfacial region.

For films of thickness greater than several atoms or chemical groups, the distribution of characteristics as a function of distance from the surface can be of interest. This type of characterization is usually called depth profiling. Monitoring film characteristics as a function of lateral location on the surface is referred to as imaging. An ultimate goal in surface analysis is to obtain three-dimensional characterization, including both lateral and depth distribution of important features.

The most tractable analyses are those involving isolated samples and unlimited sampling time. However, the most significant problems (real world) are usually those involving a sample surrounded by an ambient fluid (gas or liquid) environment in which sample characteristics are highly time-dependent. Challenging examples for characterization are lubricant films on a metal sheet during a rolling operation and a growing polymer film on an electrode during electropolymerization. In this respect, an ultimate goal from surface/thin-film characterization is to develop real time measuring capabilities, that is techniques for following time-dependent changes in a sample directly (in situ) in a processing or service environment. An additional challenge for "on-line" production environments arises when the sample is continually moving (e.g., a rolling operation), and the alignment of the analytical probe must be dynamic.

All the above analysis goals are summarized in Table 1.

III. REVIEW OF THE PRINCIPLES OF IRS

A. Theory of IRS

All energy spectroscopies (as opposed to mass spectroscopies, etc.) involve transitions between energy levels of a given system with accompanying emission or absorption of a quantum of energy in some form. Infrared spectroscopy typically refers to emission or absorption of infrared photons. Almost always this process involves transitions between vibrational quantum states, so IRS is typically a vibrational spectroscopy, although other processes such as electronic excitation of narrow bandgap semiconductors can occur at infrared frequencies. Photon spectroscopies that probe these vibrational

Table 1. Ultimate Goals for Characterization of Surface/Thin-Film Structures and Compatability with Infrared Spectroscopy Probes

	Average Compatibility of IRS with Characterization Goal		
Characterization Goal	Good	Poor	None
Coverage, film thickness, density	X		
Atomic composition			X
Chemical composition			
Chemical bonds or groups	X		
Valence states of metals			X
Bond or group orientation	X		
Molecular fine structure (conformations, etc.)	X		
Ordering		X	
Surface/film bonding	X		
Defects		X	
Impurities		X	
Depth profiling		X	
Imaging			
≤ 1-μm scale			X
≥ 10-μm scale	X		
Real-time analysis	X		

transitions by more complex mechanisms than simple absorption and emission include Raman scattering, sum frequency generation, and various other nonlinear techniques such as Raman gain and coherent anti-stokes Raman scattering (CARS). In addition, vibrational transitions can be probed using the kinetic energy and momentum of particles other than photons; in particular, electrons, helium atoms, and neutrons can be scattered from molecules and surfaces to obtain vibrational spectra. Thus, a number of ways exist for obtaining vibrational spectra of surfaces and films; IRS is just one of the choices. However, IRS can safely be said to be the most generally useful technique by far because of experimental and interpretive simplicity. IRS should be viewed as the overwhelming choice for solving practical problems.

The physical mechanism of IRS is well understood for the elementary case of a photon-electron dipole transition. To clarify the later discussion of spectroscopy at interfaces, the simple mechanism for an isolated molecule in free space is presented very briefly here. Either a passing photon (or, alternatively, a propagating electromagnetic wave) of IR frequency is absorbed via excitation of a given vibrational level to one of higher energy (absorption), or a photon is emitted by conversion of an exited state to a lower state. The simple description of the excitation mechanism for the photon-electric dipole transition is that when the electric field of the light varies at a frequency that corresponds to an energy very close to that of the energy level spacing, absorption of the photon becomes highly probable with the exact probability depending on the change in electric dipole moment during the transition. Further, the transition probability is directly proportional to the electric field intensity (the light intensity).

Because the probability of absorption increases directly with the intensity of the electric field of the propagating electromagnetic wave, a very simple quantitative relationship exists between the source intensity, the fraction of power absorbed by the sample, and the inherent transition probability or cross section. For a low density of noninteracting molecules in the sample beam, this leads to an ideal Beer's law type of relationship:

$$I/I_0 = e^{-\varepsilon c \ell} \qquad (1)$$

where I is the power transmitted with the molecules present, I_0 is the power transmitted with the molecules absent, ε is the extinction coefficient (an absorption cross section), c is the volume concentration of the molecules, and ℓ is the path length of the light beam that contains the molecules. The emission process is correspondingly simple. A freely radiating oscillator (electric dipole) generates a given intensity of light (in all directions) as a function of the equilibrium temperature of the molecule and of an inherent fixed probability (cross section) of radiation.

B. The Infrared Spectroscopy Experiment

To carry out the simplest IRS experiment, one requires several key components. For an absorption experiment, these include a source of IR radiation of variable frequencies, a radiation detector, and a mechanism for separating the response of the sample for each frequency interval of light (monochromatic response). To set up this simple experiment, there are a large number of options. The most useful ones, with their advantages and disadvantages, are given in Table 2. By far, the most cost-effective combination for the majority of surface/thin-film analyses that involve mid-IR frequencies is a blackbody-type source, a Michelson interferometer, and a photon semiconductor detector. Usually the specific items are a ceramic glo-bar (peaked at ~ 10-μm energy), one of several variations of interferometers and a HgCdTe, liquid nitrogen cooled detector. This type of combination is available commercially from several sources (a typical "Fourier transform" or Fourier transform infrared [FTIR] instrument). However, one should note that other specific combinations of components in some limited number of cases may solve critical analyses problems better than typical commercially available instruments.

IV. Infrared Spectroscopy at Surfaces and Interfaces

A. Theory

There are two major points to be made in this section. First, for solid, multiphase samples, such as metal or nonmetal overlayer film on a massive substrate, the spectra can be highly complex and very difficult to use for quantitative analysis of structure and thickness. Second, for the particular case of a planar, parallel layer sample, the spectra can be quantitatively understood in terms of layer thickness(es) and orientational ordering (if present) provided that all the necessary optical properties of the constituent layers are known.

In contrast to IRS of an isolated molecule, the experiment involving a solid material is significantly more complex with regard to the shapes of spectral features and the quantitative relationships between the number of oscillators (groups) present and the spectral intensities. There are two main reasons. The first is that the distribution and structure of vibrational levels is quite complex because of the interactions between the onstituent atoms and groups in the solid. This effect is specific to each type of sample and is not of concern in this more general discussion. The second reason, and the one of

Table 2. Summary of Major Selected Advantages and Disadvantages of Instrumentation Components in an IRS Experiment

	Advantages	Disadvantages
IR Photon Sources		
Hot surface (blackbody)	Broad band; portable; inexpensive; stable	Unpolarized, isotropic radiation; blackbody-type distribution of intensity with wavelength; concentrated in mid-IR
Laser	Very high power; monochromatic; coherent; collimated beam; possibility for short time pulses and nonlinear spectroscopies	Moderately expensive; tunability often slow and/or inconvenient; operation very dependent on particular laser or laser combination
Synchrotron	Very high flux with collimated beam; broad band; uniform intensity at all wavelengths from far-IR to near-IR	Travel to facility required; limited access
Vapor lamp (Hg, I_2, etc.)	Portable; inexpensive; covers far-IR and near-IR much better than blackbody sources	Unpolarized, isotropic radiation, peaks in power occur at specific wavelengths associated with each source
Energy Resolution Mechanism		
Michelson interferometer plus Fourier transform	Wavelength multiplexing; high throughput; up to ~ 10^3 scans per sec at low resolutions; capable of very high resolution; highly accurate wavelength calibration from laser fringe	Ultimate speed limited by mechanical scan rate, requires FT computation
Monochromator, scanning	Can measure single wavelength element data over extended period of time	Slow; high resolution difficult
Monochromator plus an array detector	Capable of very fast measurement—limited by detector speed; no moving parts	High resolution difficult; narrow band capability only
Monochromator plus Hadamard transform masks	Fast; similar to an interferometer	Requires mask sequencing and computation of data via Hadamard transforms

Table 2. Summary of Major Selected Advantages and Disadvantages of Instrumentation Components in an IRS Experiment (Concluded)

	Advantages	Disadvantages
Detector Type		
Semiconductor, photon activated (photoconduction or photovoltaic)	Can be very fast (~ps, but μs-ms typical operation) depending on specific material; extremely sensitive; low noise	Moderate to narrow bandwidth; nonlinear response at high flux
Bolometer (resistive)	Broad bandwidth operation, good in far-IR	Slow (< 1 kHz); lower sensitivity than photon detectors
Thermocouple (voltage)	Broad band; highly linear over wide flux range	High sensitivity only by direct sample contact at low temperatures
Pyroelectric (polarization)	Broad band; highly linear; inexpensive	Slow (≤ 1 kHz); lower sensitivity than photon detectors
Photoacoustic	Sensitive; favorable dynamic range (measures only absorbed radiation); no optical coupling to sample needed	Direct contact or extremely close proximity to sample needed; response can be frequency-dependent for modulated signals (FTIR, etc.)

interest here, is that the interaction of the electromagnetic wave with the sample gives rise to a transmitted component, a reflected component, and a diffusely scattered component [6]. Most important, the character and fractional contribution of each of these components is governed by a nonuniform distribution of electric (and magnetic) field strengths throughout the sample. This distribution is the result of standing waves generated in the sample. A simple (and proper) analogy for this distribution is the constructive and destructive interference that occurs when light is reflected between parallel positioned mirrors. The spectral phenomena are dependent on the nature of the sample, including the geometry and material composition, and on the measurement variables, including the wavelength and polarization of the light, the angle of incidence on the surface for an absorption experiment, and the viewing angle and polarization of the emitted light for an emission or scattering experiment. The common sample structure for which precise quantitative description is easiest is a planar sample consisting of parallel layers, each of variable thickness and uniform composition. For this structure, the exact distribution of electric field intensities throughout the sample can be determined provided that each of the materials in each layer can be assigned accurate values of frequency-dependent dielectric or optical functions. In the latter description, the appropriate values are the refractive index and absorption coefficient, n and k, respectively. When $k > o$, infrared absorption (or emission), spectral features will arise. From the ratios of the intensity values of the input electric field intensity of the light at the sample surface and the output fields at the front and back surfaces of the sample, the reflectivity (R) and transmissivity (T) (for a transparent substrate material) can be determined. The calculation of R and T over a range of wavelengths constitutes a spectral simulation. When the simulation exactly matches an experimental spectrum, the congruence implies that the sample structure is characterized quantitatively. The k values for a given vibrational transition contain the physics of the photon-electric dipole interactions. With respect to formulating the latter, there are two points to note. First, the distribution of electric fields within a given layer will vary depending on the values of n and k and the thickness for all the other layers. Thus it is not always possible to obtain simple relationships between spectral intensities and layer thickness for a given layer without understanding the entire sample structure in detail. Second, k is directionally dependent. The photon-dipole transition depends on an electric field with an associated direction (a vector) interacting with an oriented electric dipole (a vector). The interaction is thus directionally dependent (a scalar product maximized when the field and dipoles are parallel), and to correctly describe the absorption (or emission) properties of the material phase, the quantities n and k must have directional character. Mathematically, this is done by describing these quantities in the form of a tensor. Thus for samples containing IR active layers, the layer orientations are a variable affecting the nature of the spectra. For isotropic (nonoriented) layers, n and k are simple scalars, but as the net degree of orientational ordering increases, n and k become more tensor-like quantities with the full description reached at complete biaxial symmetry (a single-crystal layer with different responses along orthogonal directions). The above principles are presented in detail in a recent publication [7].

B. Experiment

There are a variety of experimental methods for which IR radiation can be directed to and/or away from a sample to perform a spectroscopic measurement. These methods can be classified into distinct types or modes. Each of these modes can be used to characterize surfaces and thin films, and each displays strengths optimized for different types of sample structures. Table 3 gives a list of modes that have been used over the years and important characteristics associated with their utility. For a given combination of mode and sample configuration, the ability to quantitate structural features depends on the ability to apply electromagnetic theory accurately as outlined in the above section. There are several sample features for which analysis is only possible, because of theoretical or practical limitations, using certain sample types and experimental modes. Five important sample features are film thickness, molecular orientation, lateral distribution of sample features, depth distribution of sample features, and substrate/film binding. Table 4 combines the above information to provide a description of which types of IRS experiments are useful for specific sample types and features. In the discussion below, each of the IR experiments is considered in detail. A general point to be made with regard to instrumentation is that typically good FTIR systems operating in the mid-IR range under medium resolution conditions can provide $\geq 0.1\%$ precision in intensity per scan. The signal-to-noise ratio can be increased by up to nearly two orders of magnitude by signal averaging. This level is more than sufficient to detect monolayer quantities of a film, even for nonoptical sampling conditions. Some recent examples of applications of IRS to monolayers are available [8,9].

1. Transmission

The transmission experiment is by far the most well known of all modes. It has a long history of application to the analysis of gases and liquids. Because detection depends on transmitted light, the sample must be somewhat IR-transparent. For solids, the sample typically consists of an absorbing powder dispersed in a transparent matrix (e.g, a KBr pellet); a very thin, unsupported absorbing film (e.g., a 2-μm polymer film); or a very thin film supported on a transparent substrate (e.g., a monolayer on a Si wafer). Detection and quantitative analysis of moderately absorbing monolayers in the latter sample configuration can be considered routine for good quality commercial instrumentation, for the case of very smooth, planar substrates. Rough surfaces scatter light and reduce the signal/noise as well as the researchers' ability to perform quantitative analysis. Curved or nonplanar surfaces distort the beam and also reduce quantitative capabilities. In all absorption spectroscopy experiments, the analyses critically depend on reliable reference spectra, e.g., a "clean" silicon wafer as a reference for a monolayer covered wafer. Differences in optical characteristics of a few parts in 10^4 or so between the sample and reference substrates can provide damaging spectral artifacts so sample/reference strategies are extremely important

Table 3. Modes of Obtaining IR Spectra for Surfaces and Thin Films

Mode	In situ for Liquids	Appropriate Sample Configuration	Special Spectrometer Configuration Requirements	Advantages	Monolayer Sensitive	Special Disadvantages
Transmission	No	1. Film on transparent window 2. Dispersed powder in transparent matrix	None	- Simple experiment - Easily quantitated	Yes	None
External reflection	Yes	Film on planar, reflective substrate, usually but not necessarily a metal	Variable angle optics	- Moderately simple experiment - Quantitated with computer calculations using EM theory	Yes	Transparent substrates are difficult
Internal reflection	Yes	Film on transparent internal reflection element (rhombohedral or cylindrical-conic)	Variable angle optics	- Moderately simple experiment - Quantitated with computer calculations using EM theory	Yes	Narrow selection of available IRS elements—may not be the substrate of interest
Diffuse reflectance	No	Powder dispersed in transparent powder matrix	Collection-refocusing optics	- Moderately simple experiment	Yes	Only powders are useful
Photoacoustic	No	Powder or film on substrate	Acoustic detector attached to or very near sample	- Moderately simple experiment	Yes	Highly specialized substrates and detector configuration needed for monolayer sensitivity on planar substrates
Surface electromagnetic waves	?	Film on planar, reflective, highly conducting metal substrate with prisms mounted for surface wave guiding	Variable angle optics	—	Yes	Very difficult experiment
Spectroscopic ellipsometry	Yes	Same as external reflection	Variable angle optics, polarizer elements placed in beam before and after sample	Highly precise, quantitative for planar film/substrate samples—obtain optical properties of film and thickness	Yes	Difficult experiment
Emission	No	Any sample type	Collection-refocusing optics; heated sample or cooled optical path components work best	Any shaped sample can be examined	Yes, but only for optimum experimental conditions	Cooled optics mode requires controlled environment; substrate background radiation can be a serious problem for monolayer and thin films

Table 4. IR Mode Applicable to Specific Sample Types and for Characterizing Specific Features

Description of Film and Features of Interest for Analysis	Transmission	External Reflection	Internal Reflection	Diffuse Reflectance	Photo-acoustic	Emission	Spectroscopic Ellipsometry
Substrate							
1. Geometry							
Planar	X	X	X		X	X	X
Nonplanar	X		(OK for cylindrical elements)	(Yes for powders)	(Yes for powders)	X	
2. Roughness							
Rough				X	X	X	
Smooth	X	X	X	X	X	X	X
3. Materials							
Metal		X			X	X	X
IR-absorbing nonmetal		X		X	X	X	X
IR transparent	X	X	X	X	X	X	X
Film							
1. Thickness							
Monolayer	X	X	X	X	X		X
Multilayer	X	X	X	X	X	X	X
Required Information							
1. Film thickness or coverage	X	X	X				X
2. Molecular or bond orientation	X	X	X		(Yes for planar substrates)		X
3. Lateral image ≥ 10-μm resolution	X	X					
4. Depth profile ≥ 0.5-μm resolution			X		X		X
5. Bonding to the substrate	X	X	X	X	X		X

in transmission analyses. The same can also be said, in general, for all absorption modes discussed below. The removal of these artifacts is a pervasive issue, but corrective strategies are too case-specific to be discussed in detail here. If good quality spectra are obtained, then quantitative analyses can be carried out using either Beer's law expressions (Eq. 1) as approximations or classical electromagnetic theory for more exactness. For low refractive index support materials (e.g., KBr or NaCl), Beer's law approximations are quite accurate, whereas for high index materials such as Si, errors of > 30% can result for the Beer's Law approach using peak intensity measurements. The use of integrated peak areas, however, provides good quantitation. Significant changes in peak positions and line widths also occur as a function of the support refractive index, and a classical electromagnetic theoretical approach is necessary to treat these optical effects properly to distinguish them from chemical effects [7]. There are two final points to emphasize about transmission experiments. First, depth profiling is not possible, because any sample appearing in the IR beam can absorb light, and thus there is no way to differentiate the depth location of an absorbing group in the beam. Second, lateral imaging is possible. Quite high-quality IR spectroscopic microscopes are commercially available and provide spatial resolution to near the diffraction limit (≥ 10 mm) [10].

2. External Reflection

The <u>external reflection</u> experiment is, from a practical point of view, much more common than the transmission experiment, because most overlayer films of interest for surface analysis are supported on absorbing substrates for which the transmission experiment is not possible. Most of the time, metallic substrates are encountered, e.g., copper and ferrous metal corrosion films and thin polymer coatings on metal stock for cans. For cases in which the metal substrate is planar and reflective, IR spectra can be generated by reflection off of the sample surface. Application of classical electromagnetic theory reveals that the experiments are optimally done at grazing angles of incidence (≤ 10° off grazing) with p-polarized light. Under such conditions, sufficient signal/noise can be obtained to allow detection of submonolayer quantities of material and, most importantly, the spectra can be quantitatively analyzed using straightforward theoretical techniques [7]. Less frequently encountered are cases in which films are supported on IR-absorbing but nonmetallic or weakly metallic substrates such as silicate glasses and highly doped Si semiconductor wafers. Quantitative, monolayer sensitivity analyses are also possible on these substrates using reflection techniques together with commercial instrumentation and correct application of theory both to optimize the experimental conditions and to interpret the data [7]. In general, the signal-to-noise ratio (S/N) can be as much as an order of magnitude less than for spectra of equivalent films on highly reflective, highly metallic substrates, due to the intrinsic physics of the light/surface interaction which dictate that the electromagnetic fields at the surface are less for nonmetals than for metals, given optimum experimental conditions. Again, as for transmission, the planar character of the substrate allows quantitation of molecular and bond orientation relative to the surface plane. These analyses are viable for any external reflection experiment for which the optical properties of the sample are well defined. Lateral imaging is also possible on these planar substrates using IR microscopy, but for the case of metallic surfaces, the requirement of grazing angles of incidence precludes very high spatial resolution. For nonmetallic or weakly metallic substrates, angles of incidence in the range of normal to ~ 60° are possible, depending on polarization, and reasonably good resolution can be expected, again limited by diffraction effects, as for the transmission experiment. Commercial microscope instruments are available for such measurements [10]. Finally, the external reflection technique does not allow depth profiling, because the electromagnetic fields generated at the surface extend as far away from the surface as the width of the incoming beam (usually several mm) and are too slowly varying as a function of distance to allow interpretation of the spectra in terms of vertical mapping of signal contributions at any useful distance resolution. Some recent examples of surface analyses by external reflection IR spectroscopy have been reviewed elsewhere [11].

3. Internal Reflection

Internal reflection IRS is a very specialized reflection experiment [12] which is, in general, considerably less useful than external reflection for analyzing surface processes. In the internal reflection experiment, an IR transparent material is cut into a slab (trapezoid or parallelogram) or cylindrical rod with conical ends and polished to give very smooth surfaces. By taking advantage of the phenomenon of total internal reflection [12], IR radiation is brought into one face of the element and guided through the interior along the long axis via multiple reflections. The electromagnetic field extends across the element surface into the surrounding medium and decays in intensity exponentially away from the surface with a falloff of the order of the wavelength of the light. If an IR absorbing film is located on the element surface, an absorption spectrum can be obtained for that portion of the film located within the above fall-off distance. Typical materials appropriate for fabricating the optical elements are Si, Ge, ZnSe, and various specialized commercial materials such as KRS5. Unfortunately, these materials are usually not the materials of interest in a typical analysis problem. Also, even if a given substrate material of interest is IR-transparent, it often cannot be easily fabricated into the required element. Thus, except for cases in which films of interest can be placed on a reusable, inert element, e.g., Si, internal reflection is not useful. One particularly useful case is when a soft polymer film is pressed into maximum contact with a hard, highly smooth element such as one made of Si. In this case, the surface region of the polymer can be examined up to a depth of the order of the wavelength of the light with an excellent S/N. However, if the contact of the film with the element surface is incomplete, errors in quantitative analyses will accordingly be present. The S/N for an internal reflection experiment with multiple reflections can be quite high, allowing submonolayer detection. The analyses can be carried out quantitatively with molecular and bond orientations determined relative to the element surface plane in favorable cases. From the physical nature of the optical path, it is obvious that lateral imaging is not possible, at least with multiple reflections. However, depth profiling is possible by carefully using the functional form of the decaying electric field in the film overlayer. The decay function can be varied by changing element materials and angle of incidence [12], which allows generation of a set of independent probes of spectral contributions of the film interior as a function of distance from the surface. Solution of the electromagnetic equations allows, in good cases, depth resolutions of better than tens of nanometers. In general, however, such applications are rarely feasible for practical problems. A major practical problem would be depth profiling a polymer surface region. In this case, the lack of completely reproducible, uniform element/polymer contact from element to element precludes such detailed quantitative profiling analysis, although qualitative analyses should be successful.

4. Diffuse Reflectance and Photoacoustic Detection

In cases for which surface films are to be analyzed on powders or high surface area granular materials, the techniques of diffuse reflectance and photoacoustic spectroscopy are quite applicable. Little will be said about such analysis in this paper, because these techniques are well documented for powders [3-5,13,14], and because quantitation of surface coverage, derivation of detailed structure such as molecular and bond orientation, and imaging are rendered extremely difficult because of the ill-defined analytical nature of the light/surface geometry and the distribution of sample characteristics such as surface morphology. However, two comments will be made. First, qualitative analyses of overlayer films, even monolayers, are quite simple, can be extremely useful, and can be carried out with commercial instrumentation. Second, whereas diffuse reflectance works only for diffusely scattering samples, photoacoustic spectra can be obtained, even for monolayers on highly smooth, planar substrates by attaching a piezoelectric element directly to the substrate in such a way as to very sensitively detect the acoustic pulses generated from absorption events in the monolayer during IR irradiation [15]. Such an experiment, however, is sufficiently difficult such that it should be considered a research tool rarely suitable for practical purposes.

5. Emission

Emission spectroscopy is a useful and underused mode of obtaining IR spectra [3,5,9,16]. All the above modes have referred to experiments in which spectra were obtained by measuring the fraction of light beam power absorbed by various IR active groups in the irradiated sample. However, every sample always emits a very weak but continuous IR spectrum from the decay of thermally populated excited vibrational quantum states, and this spectrum contains contributions from the same individual groups as seen in absorption. Thus it is possible, in principle, to obtain a spectrum from a film-covered sample just by admitting the radiation into an IR spectrometer. However, there are two reasons why this doesn't work well. First, the radiation is very weak at room temperature and is emitted in all directions. Second, most of the flux is useless background (blackbody-like) radiation from the substrate and the film as well with only a small fractional contribution from the IR vibrations of interest. Related to the latter point is the fact that all the parts of the spectrometer itself (mirrors, apertures, etc.) emit interfering background radiation. However, strategies have been developed to overcome these problems, primarily by using samples at substantially higher temperatures than the spectrometer and making very accurate corrections for sample background radiation by using film free reference samples. Commercial instrumentation is available for these experiments for use with heated samples. Monolayer detection is not possible by such strategies because of the large background corrections. However, it is possible through the use of cryogenically cooled spectrometers to detect monolayers on room temperature samples [9,17], but such instrumentation is not available commercially. For cases in which samples can be heated above room temperature, a major advantage of emission spectroscopy compared to reflection is that the sample can be of any geometrical shape and surface roughness. This makes the method extremely attractive for certain applications such as examining surface films on odd-shaped machine parts which, in fact, may be normally hot. Of course, such sample characteristics do not allow quantitative analyses. In general, without extreme effort, emission spectroscopy cannot be performed in a quantitative manner relative to the cases of transmission and reflection.

6. Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is really a special case of the external reflection experiment [18] in which changes in the polarization state of the IR beam are measured rather than the fraction of beam power reflected, the traditional reflectivity measurement. The major advantage of the ellipsometry measurement is that the polarization state change contains information about both the amplitude change and the phase change of the light, whereas reflectivity measurements contain only intensity information. The appearance of the additional variable of the phase shift allows two unknowns of the sample to be evaluated, e.g., sample film thickness and density, whereas reflectivity allows only one, e.g., just sample film thickness with the density evaluated independently. The calculations for ellipsometry are based on standard classical electromagnetic theory. Ellipsometric spectra have the added advantage that the large amount of data accumulated from the total numbers of spectral points can be used to accurately determine wavelength-independent sample characteristics such as thickness, density, surface and interfacial roughness, voids, and even density gradients perpendicular to the surface plane (depth profiling). This information is in addition to the normal spectral information involving chemical structure, bond orientation, and other features that affect vibrational modes and the absorption cross sections. By using the depth profiling capability, composition gradients could be measured, in principle. The best demonstrations of the power of ellipsometry as an incisive analysis tool for thin-film structures have been made for spectra obtained in the ultraviolet (UV) and visible regions [19]. Here, for example, thicknesses ideally can be measured to within 0.1 Å or better. Recently, interest in extensions into the IR region has accelerated [20-22], and commercial instrumentation is now available. However, although it is possible to obtain spectra of monolayer quantity films, because of signal/noise restrictions, it is not yet clear whether these films can be analyzed quantitatively with present ellipsometry instrumentation. For various reasons related to the basic physics of the experiment, it would appear that SE is most ideal for thin films on nonmetallic or weakly metallic substrates as opposed to highly conductive metals. In addition, because the quantitative value of the experiment derives from extremely high precision measurements, only highly smooth, planar surfaces lead to high precision analyses. However, even for rough surfaces, ellipsometric measurements are of more value than reflectivity measurements simply because of the extra information. Finally, because of the longer wavelength of the light, the ability of SE to measure thicknesses and perform depth profiling is significantly less than in the UV-vis regions, by at least an order of magnitude. In general, considering all the above points, it is always an advantage to use ellipsometric spectra rather than reflectivity spectra if possible, regardless of sample roughness or substrate material type.

V. IRS ANALYSIS APPLICATIONS, STRATEGIES, AND ISSUES

In this section, the use of IRS is mentioned for several types of applications including both the simpler ones involving "passive" types of samples in an analysis laboratory environment and the more complex, challenging ones involving "active" samples that are to be analyzed directly in a processing environment. In all cases, it will be assumed that analysis of monolayer quantities of surface films is of interest. Thicker films can be accommodated easily if monolayer quantities are possible.

A. The Laboratory Environment

This class of analysis covers samples that have been removed from the processing environment and have no special time limits or environmental requirements associated with the analysis.

Powders can easily be analyzed by diffuse reflectance, transmission, or photoacoustic methods with the particular method chosen depending on the exact nature of the material. Small objects can be analyzed individually by IRS microscopy if the objects are larger than ~ 10 μm in diameter. For powders and small objects, quantitation of coverage and film structure is not to be expected.

Sheet materials can be analyzed by transmission for IR transparent materials and by external reflection for nontransparent ones. As the degree of surface roughness decreases and the degree of surface planarity increases, the degree of quantitation of film coverage and structure increases. Reasonably good quality results can be expected for shiny metal sheet such as aluminum and steel alloys. The presence of occasional surface scratches that occupy less than several percent of the surface area will have little effect on the analyses, including even spectroscopic ellipsometry. It is also possible to analyze surface films on IR-absorbing sheet such as polymers, particularly if the spectral contrast or difference between surface films and bulk is large. The application of external reflection, and particularly spectroscopic ellipsometry, to high-quality polymer sheet surface analysis has been highly underutilized. However, it must be pointed out that rigorous application of interpretive theory to these analyses is necessary for quantitation.

Finally, the case of analysis of large irregular objects presents a challenge, because the above methods are only marginally applicable at best. The use of IRS microscopy in the reflection mode is one possibility if the sample is sufficiently small to fit in the microscope. However, quantitation of the spectra, while not impossible, is very difficult because of the complex optical conditions and irregular surface shapes. All irregular objects are capable of analysis by emission spectroscopy. However, in order to generate analyzable spectral features attributable to the overlayer film, the object must be heated, the film must be substantially thicker than one monolayer, and the substrate must not emit strong interfering background spectral features. It appears that the emission technique is probably underutilized for surface analysis.

B. The Processing Environment

Analysis in the processing environment brings up two additional requirements not associated with laboratory analyses as described above. The first is the ability to analyze directly in the presence of a liquid or gas medium surrounding the sample and the second is the ability to analyze in real time, a particularly severe requirement if the analysis object is constantly moving on a process line. This entire class of analyses represents the cutting edge in analysis development.

The major problem with IRS analysis in gas and liquid media is that most of the common media are highly absorbing of IR radiation and thus provide large, interfering background contributions to the analysis spectra. Examples are H_2O vapor, H_2O liquid, CO_2, and most organic solvents. When the contributions are extremely large, such as for liquid water, strategies involving corrections for the background don't work sufficiently well, and strategies involving reduction of the amount of the interfering medium generating the IRS signal are necessary. This can be done in two ways: (1) reduce the extension of the electromagnetic field from the sample surface into the medium and (2) reduce the thickness of the medium adjacent to the sample. The first can be accomplished using internal reflection and, in fact, this is the basis for several commercial IRS probes for monitoring the progress of processes in bulk liquid (or gas) reaction media [23]. However, from the point of view of monitoring real processes at surfaces, internal reflection would only be applicable when the internal reflection element could be placed within one mm or less from the sample surface, a region within the effective range of the electromagnetic field. This essentially amounts to the second strategy above, because the amount of liquid present is contained to a very small thin layer equivalent to a thin cell that could be used for external reflection or transmission. The problem with this strategy is that the internal reflection element or the infrared cell windows must be completely inert to the processing environment to prevent interfering signals arising from chemical or physical changes at these surfaces. One area in which these strategies can work is in electrochemical processing for which the electrode surface spectra can be freed of solvent and window contributions by using the unique dependence of the electrode process on the electrode potential [24,25]. A second problem of analysis in liquid and gas media is the coupling of the light in and out of the local process environment. One convenient way to accomplish this is to use optical fibers. This strategy can provide an enormous simplification in the optical path alignment and works extremely efficiently in many regions of the visible and near-IR spectrum because of the existence of high throughput, fibers with good mechanical properties. However, in the mid-IR region there are serious performance limitations with the fiber materials available [26-29] although applications have been reported [30-32].

From the above discussion, one can conclude that although IRS offers the possibility of in situ analysis of surface processes in the presence of gas and liquid media, only analysis in the presence of gases offers very realistic possibilities. Analysis in the presence of liquid media remains a case by case possibility as the feasibility depends specifically on the type of liquid and the type of surface processing. Developments of new methods of IRS analysis in this area would be of immense value.

A second important aspect of IRS processing analysis is that of analysis time. The speed of surface processing could vary in principle from microseconds to hours. Although long processing times present no problems, short processing times do. Some ideas as to possible measurement times can be obtained by inspecting Table 2, in which the time scales associated with the use of possible IRS experimental components are given. Although it is possible to operate well below the microsecond time scale by using fast laser-based systems, it is generally impossible to obtain full spectra on these time scales, because wavelength tuning of the lasers is comparatively slow. Measurements can also be done on the microsecond time scale using time-resolved FTIR, for example, through the use of step-scan instrumentation [33] now commercially available. However, in order to use this mode of time resolution, the experiment must be capable of being rerun repeatedly in exactly the same manner with the same results. This is fine for repeated pulsed experiments in the laboratory but not for one-shot processing. However, a very practical time scale of about one second is obtained by using fast, commercial Fourier transform systems. Complete spectra can be obtained in ~ 10 ms with limited resolution (~ 16 cm^{-1}) and with S/N sufficient for very thick film detection (≥ 20 nm). However, with slower scan speeds and multiple signal averaging, good resolution spectra (~ 2 cm^{-1}) of strongly absorbing monolayers in appropriate sample structures (e.g., a reflective, planar sheet metal) can be obtained on the minute time scale. This time scale is quite reasonable for monitoring typical surface processes such as photocuring, sputtering, and plasma deposition. There are ample opportunities for developments of IRS strategies and techniques in this area. The development of fast Fourier transform emission spectroscopy for heated samples would be of interest.

The final aspect of IRS analysis to be discussed is that of characterizing moving objects, a real concern for continuous, on-line processing such as sheet metal fabrication and polymer film plasma treatment. The major problem associated with these analyses, in addition to those covered above, is that of dynamic alignment of the fluctuating target area on the processing line with the positioning of the fixed, separate analysis optical line. This problem runs the gamut from the nearly intractable application of on-line spectroscopic ellipsometry, with its rigid demands of ultraprecise control of angle of incidence and beam alignment, to the very tractable application of IRS emission for which extensive movement of the sample is possible because by using very wide angle collection optics, the data are reasonably insensitive to shifts in the sample positioning. This problem is compounded by the need to match the analysis time to that of the average residence time of the target area in the analysis location. In view of the above discussion on measurement times, it appears that given very fast rolling operation speeds with possible residence times of ~ milliseconds or less for a one-cm target spot size, obtaining complete, high-quality monolayer spectra is not currently possible by a factor of ≥ 10^3. However, reasonable possibilities now exist for monitoring changes involving, for example, whether or not thick (≥ 100-nm) films are present or absent in a fast-moving target spot and obtaining some qualitative information about the physical nature or chemical composition. Development of on-line analyses is of extremely great importance, and many opportunities exist.

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4. OPTICAL SECOND HARMONIC GENERATION STUDIES OF ADSORPTION, ORIENTATION, AND ORDER AT THE ELECTROCHEMICAL INTERFACE

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ABSTRACT

The chemistry of solid-liquid interfaces affects a wide variety of important scientific and technological areas such as electroanalytical chemistry, heterogeneous catalysis, solar energy conversion, tribology, chemical sensors, and biological membranes. In each of these systems, a very small number of molecules at the surface can often control the macroscopic properties and direct the overall reactivity of the device or structure. For this reason, spectroscopists are interested in devising methods of monitoring the chemical and physical structures of such interfaces. A challenging problem for studies at condensed-phase interfaces is distinguishing between solution and interfacial species; this problem is particularly difficult for optical methods, given that the light employed in spectroscopic studies normally possesses a wavelength hundreds or thousands of times greater than typical interfacial distances.

Optical second harmonic generation (SHG) is an inherently surface-sensitive technique for studying the interface between two centrosymmetric media that overcomes this distance disparity. The remainder of the paper gives further examples of where SHG can be applied. It summarizes work under the headings "Resonant SHG Studies of Molecular Orientation, Nonresonant SHG Studies of Chemisorption, SHG Studies of Ordered Adsorption at Single Crystal Surfaces, and Future Extensions."

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5. ANALYSIS OF INTERFACES USING SECOND HARMONIC GENERATION AND SUM FREQUENCY GENERATION

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I. INTRODUCTION

The intent of this paper is to familiarize the reader with the analysis of interfaces using the generation of new frequency components (second harmonic generation [SHG] and sum frequency generation [SFG]) at that interface. There are numerous excellent reviews [1-5] that go into considerable detail describing the theoretical basis for these phenomena and that also focus on the application to certain classes of problems (such as the gas-solid interface, the electrolyte-electrode interface, insoluble monolayers at the air-liquid interface, etc.). I will touch briefly on the theory behind the phenomena, if only to provide a vocabulary, then give as many examples of applications as possible, in the hopes of stimulating the reader to think in terms of expanding these to include new problems. This is not intended to be an exhaustive list of such applications, but is rather a selection derived from the author's idiosyncrasies, with the anticipation it will serve the need for these proceedings. If the reader finds these techniques interesting and potentially useful, he will be well served by referring to the reviews cited above.

II. BACKGROUND

I am reluctant to describe this section as theoretical. However, my experience is that it is beneficial to provide those who have not actually practiced nonlinear optics with a basis for discussion of the measured quantities and their origin. I will use a minimum of equations, hoping rather to describe phenomena in words to give the reader a feeling for the processes in question. A rigorous treatment of nonlinear optics is given in Prof. Shen's book [6].

Light interacts with a medium via a polarization caused by the presence of the optical electromagnetic fields. The amplitude and phase of this polarization is determined by the susceptibility, a property of the material. At low intensity, the polarization is described by the linear susceptibility and leads to the familiar dielectric constant, a complex quantity manifest as the refractive index and absorptivity of the material. However, at higher intensity, the polarization can become nonlinear in the incident fields and must be described by including the higher order material susceptibilities. Because the nonlinear polarization results from products of the field components, the net polarization will now contain frequency terms at sums and differences of the frequencies of the incident fields. This gives rise to the rich spectrum of phenomena described as nonlinear optics, which includes multiphoton absorption, self-focussing, sum and difference frequency generation, hyper-Raman scattering, and many other effects.

The electromagnetic fields of the light are vector quantities, therefore the material susceptibilities that couple them are tensors and must reflect the symmetry of the medium. The lowest order coupling, of two optical fields, is mediated by the second order susceptibility, which is a third rank tensor, and which must, as a result, be nonzero only where there is no center of symmetry. This explains, for example, why crystals used for frequency doubling and for sum- and difference-frequency mixing are not centrosymmetric. It also demonstrates the basis for the utility of frequency mixing at surfaces: when two centrosymmetric media are in contact, the second order susceptibility vanishes except at the interface. Thus, the bilinear (two at a time) coupling of frequency components can be used as a probe of a material quantity that endures only at the interface.

The experiment to probe the pairwise coupling of incident frequency components at an interface is conceptually quite simple. In the easiest case, a single high-intensity pulsed laser beam is focussed at the interface, at a power density low enough to prevent sample damage. The incident field has a well-defined propagation direction, so when it couples with itself to form the second harmonic (twice the frequency) via the second order susceptibility at the interface, the induced dipole will radiate only in one direction due to momentum conservation. Thus a new beam is created at half the wavelength of the incident light, whose intensity can be measured by chromatic separation and suitable detection. When two different colors are used, four new frequency components are created, at the harmonics and the sum and difference frequencies, but each is still a well-directed beam that can in principle be treated as above for isolation and detection. Because the interaction length for pairwise coupling is very small compared to the wavelength of light, there are no problems due to phase shift between the fundamentals and the generated frequencies, but for this same reason the efficiency of generation is very low, typically one photon for every 10^{12} to 10^{16} incident. Nonetheless, because of the chromatic and directional purity of the generated beams, one nearly always has sufficient intensity to perform an experiment.

The induced dipole, which is the source of the generated light, is the product of the incident field amplitudes and the coupling susceptibility. The detected intensity is the square of this amplitude, therefore it is proportional to the squared modules of the susceptibility. Any susceptibility is a complex material property that manifests the energetics of that material in its wavelength dependence. Consider as an example the linear susceptibility. An electric dipole allowed (one photon) transition will cause the imaginary part of the susceptibility (the absorptivity) to increase to a maximum, determined by the width and oscillator strength of the transition, for a photon energy resonant with the transition energy. The real part of the susceptibility (the enhancement of the refractive index above the vacuum) goes through a sign change at this energy, from a positive contribution at lower energies to a negative contribution at higher energies. An experiment that is sensitive to the squared modules of the susceptibility thus sees a smoothly rising intensity as a function of photon energy from above and below, to a maximum at the resonant energy of the transition. The second order susceptibility includes resonances with all the input and output photon energies, which give structure to the spectrum of generated intensity versus fundamental or generated wavelength.

It would be remiss of me to proceed without mentioning that the discussion above is a somewhat idealized picture of the generation of new frequencies by nonlinear reflection from a surface. In particular, some second harmonic (SH) intensity arises from the nonzero third order susceptibility of the bulk of the materials forming the interface. In the point dipole picture (fields only interact at a point by their dipole fields at that point), this contribution is zero, but if the field gradients are included (nonlocal interactions), the third order susceptibility can couple two fields and a gradient to form a bilinear frequency sum. The weakness of this interaction is mitigated by the fact that it is integrated over the penetration depth of the optical fields into the medium, which can be hundreds of times greater than the interaction length of the surface process. However, generally this forms a background that is not affected by surface modification and does not interfere as a practical matter [7,8].

For surface nonlinear optical spectroscopies, the resonances described above are between material states at the interface. That is, the intensity of the generated light is determined by the electronic and vibrational properties of the species at the surface, and gains utility as a means of measuring these properties and the changes they undergo due to surface modification. Usually, transitions between electronic states are about 1 to a few electron volts (eV) and are probed by the photon energy of the fundamental or the second harmonic in the SHG experiment. Transitions between vibrational states range from hundredths to tenths of an eV (tens to hundreds of milli-electron volts, meV), and are probed by an infrared photon in the SFG experiment. Examples of both of these experiments will be described below.

Finally, I will conclude this section with a brief historical note. The nonlinear optical properties of a surface were first considered in 1962 [9], shortly after the demonstration of the first optical maser (laser). In a few years, nearly every nonlinear optical phenomenon had been observed, and surface SHG was not an exception [10]. Indeed, the sensitivity of SHG to submonolayer quantities of adsorbates was demonstrated by 1969 [11], but this work went unnoticed. When SHG was used to probe the optical properties of a silver electrode used for surface-enhanced Raman scattering [12], it was realized that the technique was sensitive to small fractions of a molecular monolayer even without the enhancement of surface roughening [13]. This has led to the development of SHG as a general surface probe.

I will summarize a few important facts for the reader to carry to the rest of this presentation. One (or two) intense laser beam(s) incident on the interface between two media, each of which is (bulk) centrosymmetric, results in the generation of new beams at the second harmonic and sum/difference frequencies of the incident beams. The coupling of the frequencies is mediated by the second order susceptibility, a material property that vanishes by symmetry everywhere except at the interface. The intensity of the generated beams is proportional to the squared modules of the second order susceptibility, which has maxima at photon energies of the incident and generated light that are resonant with electronic and vibrational transition energies of the interface species. Furthermore, the susceptibility is a tensor quantity that must transform as the point group of the interface, thus it is sensitive to any anisotropy or orientational pattern in the plane of the surface.

III. APPLICATIONS OF SURFACE NONLINEAR OPTICAL SPECTROSCOPY

A. SHG

The last paragraph of the preceding section can be summarized as the following equation:

$$I(2\omega) \propto |e(2\omega) \cdot \chi \cdot e(\omega)\, e(\omega)|^2\, I^2(\omega), \tag{1}$$

where I is the intensity, χ is the susceptibility, e is a polarization vector, and ω and 2ω are the fundamental and second harmonic frequencies, respectively. When the surface of a substrate, s, is modified by the addition of an adsorbate, a, the net susceptibility can be expressed as

$$\chi = \chi_s + \chi_a + \chi_I , \tag{2}$$

where χ_I represents the change in susceptibility caused by the substrate-adsorbate interaction. All applications of SHG utilize the change in susceptibility caused by adsorption, either as the additional susceptibility of the adsorbate itself or that due to the interaction with the substrate. Usually, the substrate susceptibility for metals and semiconductors is much larger than that of the adsorbate, so the change in SH intensity due to surface modification is that ascribed to the interaction of substrate and adsorbate. On the other hand, the contributions of substrate and adsorbate are comparable for dielectrics, and the interaction is negligible. I will describe a number of examples of each interaction, for cases of solid-gas, solid-liquid, and gas-liquid interfaces involving metals, semiconductors, and dielectrics.

Metal and semiconductor surfaces in ultrahigh vacuum (UHV) provide a prototypical system for the use of SHG to probe a surface subjected to modification by adsorption [14,15]. The substrate can be prepared as a well-ordered crystalline surface, and both it and the substrate-adsorbate system can be analyzed using the full arsenal of UHV surface spectroscopies. Thus the SH intensity can be correlated with changes in the structure and energetics determined by other means. Furthermore, the high reflectivity of most metals leads to a large transverse optical field, the source of appreciable SH intensity. A clean, well-ordered single crystalline metal surface is anisotropic in the plane of the surface due to the crystalline ordering. When the plane is not centrosymmetric, this anisotropy is evident in the dependence of SH intensity on the rotation angle of the input polarization, in normal incidence [16], or of the substrate about its surface normal for p-polarized, off-normal incidence, as shown in Figure 1. In this case, because the SH intensity includes contributions from both isotropic and anisotropic elements of the susceptibility tensor, the C_{3v} symmetry of the surface causes a three-fold symmetric rotational pattern of SH intensity [15].

Many clean metal surfaces have unoccupied surface electronic states in the gap between the Fermi energy and the vacuum level [17]. Resonances between the experimental photon energies and transitions connecting occupied and unoccupied surface states lead to maxima in the susceptibility. These surface states are quenched or shifted when adsorbates are chemisorbed to the surface, which causes a reduction in SH intensity with coverage, as shown in Fig. 1 for the adsorption of hydrogen onto the Ni(111) crystal face. Indeed, it is possible to account quantitatively for the coverage dependence of the susceptibility, at least phenomenologically. These data are typical of many in the literature. However, it is also possible for the adsorbate to shift the electronic transition into resonance with the fundamental or second harmonic, as is the case for hydrogen on platinum [18].

Studies of semiconductors in UHV are quite similar to those of metals. The common technologically important semiconductors are silicon and germanium [18-25]. Both are centrosymmetric, and both have been studied using SHG, with the bulk of the effort, by far, devoted to silicon. Single-crystal surfaces of silicon have been used as substrates to study hydrogen adsorption [24], thin-film oxide formation [19], and the utility of SHG as a monitor of surface cleaning [26]. Additionally, because of the technological significance of metal-semiconductor contacts, metal overlayers on silicon have been probed using SHG [21,22,27]. In the case of a nonreactive metal such as gold, the rotational pattern was seen to change as a function of multilayer coverage and was ascribed to a change in the symmetry of the gold-silicon interface viewed through the few-monolayer-thick metal overlayer [22]. Recent work on the nickel/silicon system, which forms nickel disilicide, has shown that the SHG contribution from the silicide/silicon interface can be distinguished [27]. Also, an electronic transition at the Si(111)/CaF_2 interface has been found using SHG [28].

Finally, SHG is being used to study the surface diffusion of adsorbates on both metals and semiconductors. Carbon monoxide on both Ni(111) and Ni(110) has been reported [29], as has hydrogen on Si(111) [23].

Considerable effort has gone into the use of SHG to probe the modification of metal surfaces by electrochemical deposition. A real synergy exists between the diagnostic technique and the surface modification technique. Traditional analytical techniques of surface science can't be applied in situ, because they require UHV conditions, whereas the electrolyte is transparent to the fundamental and harmonic beams. Also, electrochemical deposition is a technologically significant technique whereby a metal surface can be modified controllably and reversibly, and the surface coverage can be measured independently by the integrated charge passed by the cell.

The electrode in contact with an electrolyte was among the first systems to be studied using SHG [10]. The change of SH intensity with bias voltage was interpreted as arising from a change in surface charge at a featureless conducting sheet (the electrode) due to either deposition or capacitive charging. Recently, however, recently extensive work comparing SH intensity from single-crystal electrode surfaces with similar surfaces in UHV has shown the situation to be more complex [3,30-33]. The rotational anisotropy and wavelength dependence of SH intensity are similar to those seen in UHV, and for those cases in which adsorbate formation can be affected both by electrochemical deposition and by gas phase adsorption (for example, hydrogen on platinum) [18,34], the coverage dependence of SH intensity is similar. This implies that the surface states of clean metals are not completely quenched at a metal electrode, and overlayer formation by electrochemical deposition may cause SH intensity changes via mechanisms similar to those in UHV. Certainly, the complexity of potential dependence of the SH intensity from an electrode surface remains a rich source of current research.

Despite the uncertainties indicated above, SHG is a valuable technique for monitoring the surface of an electrode in contact with an electrolyte. Formation of submonolayer quantities of metal overlayers by underpotential deposition causes a considerable change in SH intensity [35], as does charging of the surface with adsorbed hydrogen prior to the evolution of hydrogen gas [36]. Another important aspect of electrochemical modification of surfaces is the adsorption of charged organic species from the electrolyte. SHG can also be used for such systems, and because of the structure of the adsorbate, even more information can be gleaned on the electrode-adsorbate system. The susceptibility contribution from the adsorbate, χ_a, for organic species can be appreciable. For the chromophobe methylene blue on platinum, selection of a probe wavelength resonant with a molecular electronic transition permitted the determination of the orientation of the molecule versus coverage on the electrode surface [37].

The application of SHG to the analysis of dielectric surfaces is somewhat different from that of metals and semiconductors. The only surface states of dielectrics are similar to those of molecules; that is, they are spatially localized and characterized by rather narrow resonances. χ_s and χ_a are comparable, and usually the change in SH intensity due to surface modification by adsorption at a dielectric is caused not by the interaction susceptibility, but rather by that of the adsorbate. Most adsorbates studied have been organic chromophores, which have a well-known, polarized optical transition that is resonant with the photon energy of the fundamental or second harmonic. SHG is used to follow the adsorption process, and the polarization dependence of the resonant SHG is used to determine the orientation of the transition dipole of the chromophobe, and thus of the molecule on the dielectric surface.

At the solid-gas interface, most examples are of dye molecules externally coated onto a substrate (e. g., by spin coating). At the solid-liquid interface, adsorbed chromophores have been used to measure the kinetics and thermodynamics of adsorption from solution, and to determine the orientation of these molecules at the interface [38]. At the liquid-gas interface, both soluble and insoluble species have been probed. Molecules in solution that are at the liquid surface instead of in the bulk have been shown to have preferred orientation and to undergo different reaction dynamics from those in the bulk, because of the anisotropy of their surroundings [39]. Insoluble monolayers can be formed at the surface of water as Langmuir-Blodgett (LB) films. SHG studies of LB systems have demonstrated surface-pressure-dependent orientation, two-dimensional thermodynamics, and surface photolysis [5].

B. SFG

There have been considerably fewer studies using SFG than SHG. To probe electronic properties of the interface, SFG is useful to define an intensity maximum as arising from a resonance with the fundamental or the generated beam [28], but eliminating this ambiguity only infrequently justifies the added complexity. On the other hand, SFG is critical in probing the vibrational structure at an interface. In principle, vibrational spectroscopy is possible in SHG using an infrared (IR) beam as the fundamental probe, but the problem of detection is inseparable. The net conversion efficiency of a surface nonlinear optical process requires that detection be effected with single-photon counting sensitivity. This is not possible with present IR detection techniques, so the dependence of surface susceptibility on vibrational degrees of freedom must be shifted into the energy regime accessible with photomultiplier tubes, which requires summing the IR frequency with that of a visible laser.

The application of SFG to the analysis of surface species has been limited mostly to LB films and self-assembled monolayers at a metal surface. Studies of the former system demonstrated the ability to distinguish between different vibrations involving C-H bonds, showing the capability for chemical specificity and determination of chemical bond orientation at the interface [5]. SFG of molecules self-assembled at a crystalline metal surface, using picosecond pulse-width lasers, was used to probe for the first time the dynamics of excited vibrational states of molecules adsorbed at a metal surface [40].

Let me summarize by drawing some general practical conclusions concerning surface SHG and SFG. Both techniques utilize an agonizingly small efficiency of generating new frequency components as essentially invisible beams that must be separated and detected, and whose intensity must be monitored to determine the effects of surface modification. However, in most cases, light of the appropriate color can be found to which the intervening medium between the interface and observer is transparent; this generates enough light via a resonance with the susceptibility to be detectable, and provides valuable information concerning the state of the interface during submonolayer surface modification. SHG primarily provides information on the electronic degrees of freedom of the interface, while SFG, although a more complex experiment, provides information on the vibrational structure, which is of a truly chemical nature.

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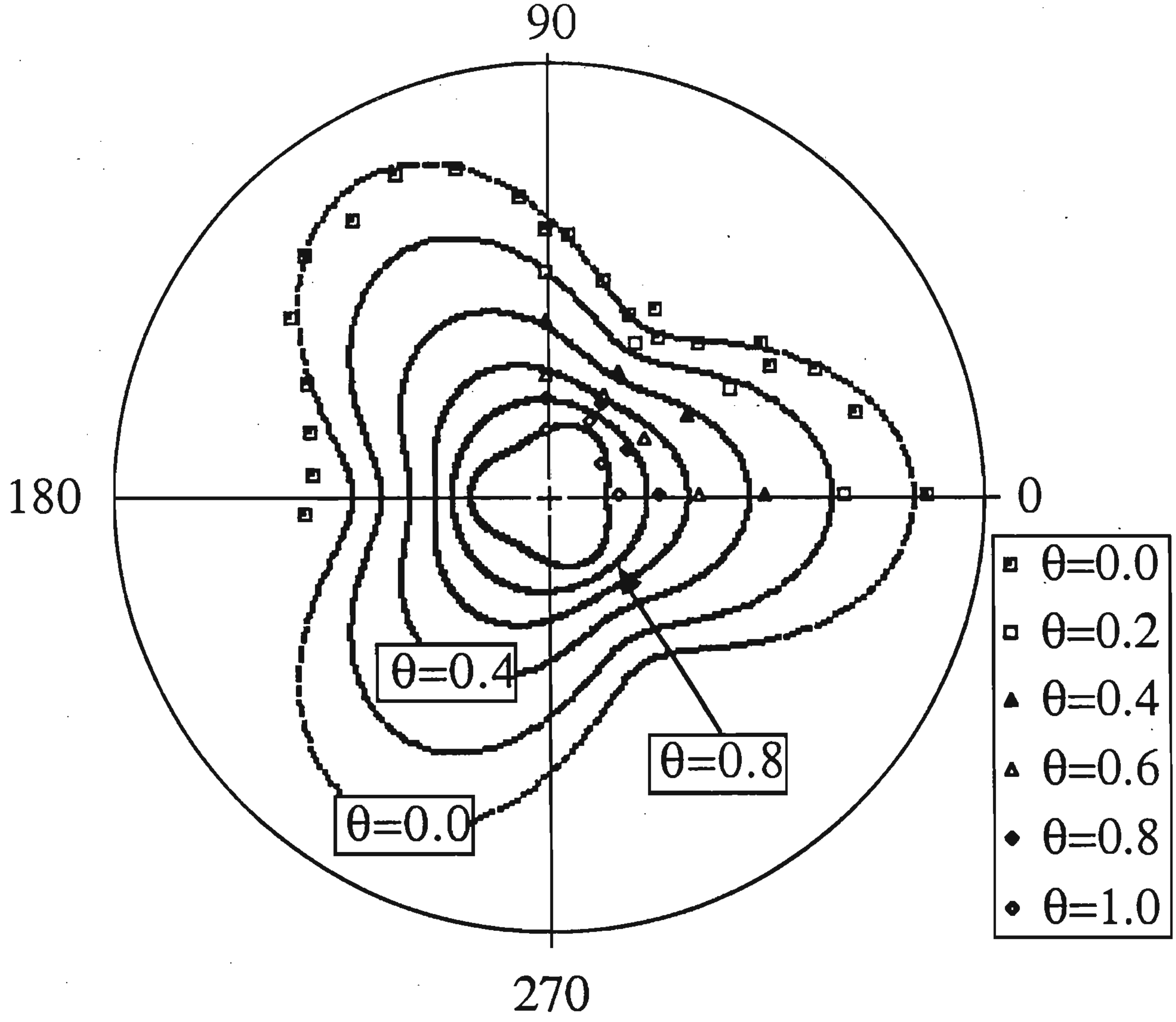

Figure 1. Continuous curves show the calculated square root of the SH intensity (proportional to $\chi^{(2)}$ as a function of azimuthal angle, ψ, for hydrogen coverages, θ = 0.0., 0.2, 0.4, 0.6, 0.8, and 1.0 on the Ni(111) surface. Discrete data points are shown for the clean surface (outer curve) and at inferred coverages from the adsorption/desorption data. Details are given in Ref. 15.

6. SCANNING PROBE MICROSCOPY

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ABSTRACT

Several techniques have been developed over the past decade using near-field effects to obtain high resolution microscopic images and surface microanalysis. These techniques are referred to as scanning probe microscopies (SPMs). In each of these microscopies, a sharpened probe is used to measure a specific interaction between the probe and the surface of interest. This new and expanding field of microscopy resulted from the invention of the scanning tunneling microscope (STM) in 1981 by Binnig, Rohrer, and coworkers. The STM measures the electronic interaction between a conductive (or semiconductive) probe and the sample to obtain atomic resolution images of the electronic surface structure.

Since the invention of the STM, other near-field interactions between a sharpened probe and sample have been used to image a variety of materials with nanometer to subnanometer resolution. The scanning force microscope (SFM) was developed immediately after the STM and is considered the cousin of the STM. In the SFM, various forces such as van der Waals, adhesive, frictional, and capillary forces are measured between the probe and the sample. By scanning across a sample at a constant force ($\sim 10^{-9}$ N), the topography of both conductive and nonconductive samples can be measured.

In a chapter on SPMs [1], we describe the history behind the development of SPMs and the physics and mechanics of their operation. Examples are given from the literature that mark various developmental steps. Also, several other scanning probe microscopic techniques are reviewed.

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7. LOCAL ORDER AND BONDING PRIMARILY USING EXAFS AND SEXAFS

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I. INTRODUCTION

A primary goal in understanding surfaces is determining the structural arrangement of surface atoms. Because many surface problems involve surface structures lacking long-range order, an appropriate technique for this instance is one with sensitivity to the local arrangement of atoms. One of the most widely used such techniques involves conducting surface extended X-ray absorption fine structure (SEXAFS) studies. The growth of SEXAFS as an investigative tool has largely been due to two important occurrences: the development of synchrotron radiation and the progress made in the understanding and theory of extended X-ray absorption fine structure (EXAFS). SEXAFS extended X-ray absorption fine structure is important, largely because it is a nondestructive probe and has surface sensitivity.

Because it is impossible to adequately discuss all aspects of SEXAFS in a short review like this, much detail has been omitted in the hope that the references provided are sufficient to locate other sources where that detail can be found.

II. FUNDAMENTALS OF SEXAFS

SEXAFS owes its origin to the development of the understanding and theory of EXAFS. Although first discovered more than 70 years ago [1,2], EXAFS went relatively unnoticed until Sayers et al. [3] showed that Fourier transforming the isolated data in photoelectron wave vector space could yield reliable structural results. To understand the results and developments of SEXAFS, we must first discuss the principles of EXAFS in an overly simplified manner. More detailed discussions of the physics and theory of EXAFS can be found in reviews by Stern [4] and Lee et al. [5].

EXAFS can only be detected for atoms in the condensed state. The physics behind this process is as follows: on penetration into a volume of atoms in the condensed state, X-ray photons with energies up to approximately 40 keV may undergo absorption, with the effect dominated by photoelectron absorption. In this process, a photon, having energy equal to or greater than the binding energy of a core electron, is annihilated, transferring all of its energy to the photoelectron. The photoelectron is ejected from the photoexcited atom with kinetic energy equal to the net energy of the incoming X-ray photon less the binding energy of the core state, leaving behind a core hole. For most systems, photoelectrons having low kinetic energies, typically below 30-50 eV, interact strongly with the potential of the surrounding atoms: the interaction becomes progressively weaker as the energy increases. This naturally delineates the X-ray absorption near edge structure (XANES) region near the edge from the EXAFS region above the edge. The significance of the photoelectron interacting weakly with the neighboring atoms' potential is that, theoretically, this interaction can be treated as a perturbation on the final state of the photoelectron, the initial state remaining unaffected because it is a tightly bound core state. To understand how the fine structure above the edge originates, we must imagine the photoelectron as a wave propagating outward, away from the photoexcited atom. As shown in Fig. 1, the photoelectron wave is backscattered by the surrounding atoms. The final state of the photoelectron is given by a superposition of the outgoing and scattered waves. The absorption rate is calculated quantum mechanically by a matrix element between the initial core state and the final state of the photoelectron. Because the initial core state is nonzero only at the location of the central atom, it is sufficient to determine how the final photoelectron state is affected by the surrounding atoms at the center of the absorbing atom. The fine structure above the absorption edge results from the alternate constructive and destructive interference of the outgoing and scattered portions of the photoelectron wave, thus modulating according to its final state at the location of the central atom. As the energy of the photoelectrons increases, their wavelength decreases, coinciding at certain values to integral measures of the distance to the near neighbors. Thus, in the single scattering scheme, the outgoing and backscattered waves add constructively to give a relative maxima to the final state at the location of the central atom. This implies that the probability for the absorption of an X-ray photon has relative maxima values for these particular photoelectron wavelength values, or, conversely, for X-ray energies coinciding with these values. Similarly, when the photoelectron wavelength is approximately equal to half integral measures of certain near neighbor distances, the probability for the absorption of an X-ray photon has a relative minimum. Therefore, the phase of the EXAFS oscillations depends on the distance from the photoexcited atom to the surrounding atoms, while the amplitude depends on the type and number of these atoms backscattering the photoelectrons. Assuming that single scattering events are dominant, the expression for the EXAFS oscillations is given by

$$\chi = \frac{\Delta\mu}{\mu_o} = -3\sum_i \sum_j \frac{1}{kR_i^2}\cos^2\theta_{ij}|f_i\ (k,\pi)|\sin[2kR_i + \phi_1^i(k)]\,e^{-2\sigma_i^2 k^2}e^{-2R_i/\lambda_i(k)} \qquad (1)$$

for s state excitations (K- or L_1-edges). The expressions for the EXAFS involving p state excitations (L_2-and L_3-edge) are similar to Eq. 1, but are slightly more complicated because the final state has an admixture of states having s and d symmetry. In Eq. 1, μ is the X-ray absorption coefficient, μ_o is the absorption coefficient of an isolated atom, $f_i\ (k,\pi)$ is the backscattering amplitude of the photoelectron wave, and λ is the photoelectron mean free path in the condensed matter. The index i refers to the ith shell of atoms, all at the same distance R_i from the absorbing atom, while the index j refers to the individual atoms within each shell. θ_{ij} is the angle between the X-ray electric field vector **E** and the position vector $\mathbf{r}_{ij}$ from the absorbing atom to the jth atom in the ith shell. The effect of backscattering of the photoelectron by different atomic species is described by

$$f(k,\pi) = |f(k,\pi)|e^{i\varphi(k)} = \frac{1}{2ik}\sum_l (2l + 1)\,(e^{2i\delta_l} - 1)(-1)^l \qquad (2)$$

where k is the magnitude of the photoelectron wavevector and l denotes the dipole allowed angular momentum quantum number of the final state (the final state has p-like symmetry for which $l = 1$ by the dipole selection rule). The oscillatory nature of EXAFS is contained in the sine term, within which $2kR_i$ is the phase resulting from single scattering of the photoelectron from the ith shell atoms and $\phi_1{}^i$ is given by

$$\phi_1^i\ (k) = \varphi_i\ (k) + 2\delta_1\ (k) \qquad (3)$$

where φ_i is the backscattering atom phase shift and δ_1 is the central atom phase shift experienced by the $l = 1$ photoelectron traveling through the atomic potential of the backscattering atom and of the photoexcited atom, respectively. The EXAFS oscillations undergo damping as described by the two exponential terms in Eq. 1. The first term takes into account, assuming a Gaussian distribution about the average distance R_i, the disorder due to thermal vibrations and structural imperfections of the surrounding atoms. The assumption is that the disorder is small. The EXAFS Debye-Waller factor σ^2 is similar to its namesake in X-ray diffraction, but different in the respect that it measures the disorder of each atom in the ith shell relative to the central atom position and <u>not</u> relative to the mean lattice position of each atom. The second exponential term takes into account the lifetime of the excited photoelectron state to which there are two contributions: the lifetime of the core hole (~ 10^{-15} s for the K-shell of copper) and incoherent scattering of the photoelectron by other electrons and atoms. It is this effect that is responsible for the EXAFS signal reflecting the local structure of the sample. In deriving Eq. 1, some of the assumptions made about the photoexcitation process occurring in the condensed state are that the photoelectron can be treated as a plane wave, single scattering contributions to EXAFS are strongly dominant over multiple scattering ones, and many body effects can be neglected, i.e., the photoelectron is considered an independent particle relative to other electrons in its vicinity. Unfortunately, these assumptions have, in general, proved to be insufficient for direct fitting of EXAFS spectra using Eq. 1. New advances in the theory of EXAFS (and photoexcitation in solids), notably by Natoli [6] and Rehr [7], attack this problem directly by using multiple scattering as well as single scattering formalisms, spherical waves in place of plane waves, and taking into account many body effects.

The polarization-dependent aspect of EXAFS is especially important for surface study applications. Because of the $\cos^2 \theta_{ij}$ dependence, the EXAFS signal decreases substantially as the angle between the X-ray electric field vector E and the position vector r_{ij} of the neighboring atom relative to the location of the central atom increases. Thus, by carefully orienting the surface of the sample relative to the polarization of the incoming X-ray beam, one is able to determine the geometric arrangement and type of near neighbors surrounding the central atom on the surface. The polarization dependence of L_2- and L_3- edge EXAFS is weaker than for K- and L_1-edge EXAFS due to the nature of the final states involved in the p state and s state excitations, respectively. In order to illustrate this effect, we turn our attention to the example of a chemisorbed atom configured in a threefold hollow site, as shown in Fig. 2, and calculate the term

$$\sum_{j=1}^{N_i} \cos^2 \theta_{ij}, \tag{4}$$

in a similar fashion to Stohr [8]. In this case, i = 1 refers to the first shell atoms, and the summation is up to 3, because that is the number of nearest neighbors. Evaluating Eq. 4 gives

$$\sum_{j=1}^{3} \cos^2 \theta_{ij} = 3 \cos^2 \alpha \cos^2 \beta + 1.5 \sin^2 \alpha \sin^2 \beta \tag{5}$$

For structures having threefold symmetry or higher, there exists a so-called "magic angle" (α or β = 54.7°) for which one can obtain a measure of the total coordination number for the atomic shell in question. In this way, β can be obtained from an amplitude analysis of the first shell data either by using a ratio of the experimental data to a standard or by fitting the EXAFS oscillations. Using Eq. 4, Stohr derives similar expressions in his review [1] for several of the most common atomic structural units found on surfaces.

III. DATA COLLECTION

The most straightforward way to measure EXAFS is to perform a transmission experiment: place a photon detector directly in front and one behind the sample to allow for a direct determination of the X-ray absorption coefficient $\mu(E)$. However, because transmission requires using sufficiently thick samples that preclude performing surface studies, SEXAFS studies are done using processes involving radiative and nonradiative electronic transitions associated with the annihilation of the core hole created by the photoionization process. In this section, we discuss detection techniques used in SEXAFS studies; the most common are fluorescence yield, Auger electron yield, total electron yield, and ion yield.

A. Fluorescence and Auger Yield

As mentioned above, there are two fundamental processes, involving radiative and nonradiative electronic transitions, responsible for the annihilation of the core hole created during the photoionization of the absorbing atom. As illustrated in Fig. 3, a fluorescence photon is emitted from the absorbing atom on the filling of the lower energy core hole state (1s in this example) by an electron from a higher energy state ($2p_{3/2}$). The K_α fluorescence process has the highest transition probability in the case of the K shell excitation. The background signal consists of elastically scattered and Compton scattered X-ray photons having energies higher than the K_α fluorescence photons. The Auger electron detection for SEXAFS studies was first suggested by Lee [9] and by Landman and Adams [10]. Auger emission process results when the excess energy from the higher level core electron ($2p_{3/2}$), in making the transition to an empty lower energy core state (1s), is given up to another core electron ($2p_{3/2}$) in the same shell. The background in Auger electron detection is usually due to inelastically scattered electrons. These are competing processes in which the Auger yield is the strongest for low-Z atoms, while the fluorescence yield increases at the expense of the Auger yield and becomes the strongest for high-Z atoms. Several groups have reported the dependence of the fluorescence yield [11] and Auger yield [12] on atomic number Z.

Because the probability of the creation of the core hole is equal to the absorption rate in the solid, the transition rates involving the fluorescence and Auger electron emission processes are therefore proportional to the absorption rate. The expression for the surface signal strength I_s , for a thin adsorbate layer ($\mu_s x << 1$), is given by [13]

$$I_s = \varepsilon_s I_0 \omega_s \Omega \mu_s x \tag{6}$$

where ε_s is the detection efficiency for photons or electrons, I_0 is the incident X-ray intensity, ω_s is the fluorescence or Auger electron yield, Ω is the solid collection angle, μ_s is the X-ray absorption coefficient, and x is the adsorbate layer thickness. Thus, to extract the SEXAFS from the spectra obtained by detection of I_s, we use the definition for χ in Eq. 1 [14].

Because the penetration depth for X-rays is much larger than the surface layer thickness (one absorption length is ~ 42 μm for Al at 1 keV), the background signal is, generally, almost entirely due to the bulk. In many cases of interest, specifically when the signal-to-background ratio is very small, it is necessary to use an energy-discriminating detector to enhance the signal statistics. Electron signal detection is generally more preferred than fluorescence detection for SEXAFS for several reasons: (1) Auger electron yield is greater than fluorescence yield for all atoms having Z < 30 for K-edges, and for all atoms having Z < 90 for all three types of L-edges, (2) electrons can be focused to increase the their collection efficiency, and (3) electron detectors are more compatible with the UHV environment used for surface studies than photon detectors. However, there are instances when one detection mode is preferred over the others due to complications that arise in relation to the experimental configuration and system studied. Some of these complications include so-called "Bragg" diffraction peaks and related effects contaminating the spectra, photoemission peaks entering the detector energy selection window while sweeping the incident X-ray energy, and step height (signal-to-background ratio) versus signal-to-noise ratio considerations. We discuss these and other complications in greater detail below.

Bragg peaks occur when the incident X-ray wavelength and angle satisfy the Bragg diffraction condition for the substrate or adsorbate crystalline atomic planes. Additionally, interference between the incident wave and standing wave fields, established in the sample as a result of the Bragg diffraction condition, modulates the photoabsorption to produce "derivative"-like glitches in the spectra [15]. Due to the nature of detection, fluorescence yield is much more sensitive to the Bragg peaks, while electron yield techniques are more sensitive to the derivative-like glitches. These effects become less problematic at soft X-ray energies for which the Bragg diffraction condition is not fulfilled for most substrates.

In order to understand the criteria by which a detection mode is chosen to optimize the signal, we first have to discuss sampling depths for electron detection. The manner in which the electron mean free path in solids depends on kinetic energy has been well characterized [16]. However, the sampling depth in this case is not simply defined by the consideration of the electron mean free path due to single scattering events. Inelastic scattering of high-energy primary photoelectrons and Auger electrons produces a large number of low-energy secondary electrons through a cascading process; a sizable number of these secondary electrons can escape into vacuum. This increases the sampling depth beyond the mean free path value. Jones and Woodruff [17] have estimated, from total electron yield EXAFS measurements at the Al K-edge (1562 eV), the sampling depth in aluminum metal to be 65 Å and in aluminum oxide to be 130 Å, while Martens et al. [18] estimated the sampling depth for copper metal to be 500-2000 Å at the Cu K-edge (8979 eV).

Signal optimization is carried out in terms of the signal-to-noise ratio $S_N = I_S/I$, where I is the normalized incident flux count rate and is equal to the sum of the signal plus background count rates, provided that the noise is purely statistical in nature. However, there exists, in addition to statistical noise, an instrumental noise contribution characterized by glitches or structures in I_0 that persist in the fine structure due to insufficient normalization [1,19]. The instrumental noise becomes especially bothersome for low adsorbate coverages and for low Z atoms. In this case, the signal-to-noise criteria has to be discarded in favor of signal-to-background. This was demonstrated rather eloquently by Stohr et al. [20], from a SEXAFS study of 0.08 monolayer coverage of S on Ni(100), who showed that, while the Auger-electron signal rate was higher, its signal-to-noise ratio is very comparable to that of the fluorescence signal measured on the same system. However, the signal-to-background ratio for fluorescence is about a factor of 10 higher than for the Auger-electron signal, clearly establishing in this case the criteria for merit. As demonstrated in this work, the fluorescence background signal can be lower than the background for electron detection even though the penetration depth for X-ray radiation is much greater than the electronic escape depth in solids. Stohr and coworkers attribute this, in large part, to a strong reduction of elastically scattered X-rays at lower photon energies.

Another concern is the surface sensitivity of a detection technique for the particular system being studied. There is no difference in the level of surface sensitivity for fluorescence and electron detection, with or without energy discrimination, for a system of a well-defined layer of adatoms on a surface. However, in the case of alloying, surface absorbing atom diffusion into the bulk, or a clean surface, close attention must be paid to the sampling depth for each detection technique in order to select the one appropriate for the measurement desired. As was shown by Comin et al. [21] for Si amorphisized by ion bombardment, it is possible to perform depth profiling with energy-discriminating electron detection, thus taking advantage of the dependence of the sampling depth on the energy of the primary Auger electrons.

In the remaining portion of this section, we discuss in greater detail the elastic Auger, partial Auger, and total electron yield techniques used in SEXAFS studies. A short discussion on ion desorption yield is also presented.

B. Elastic Auger Yield

As mentioned above, energy discrimination is an effective and sometimes absolutely necessary method of optimizing the signal and enhancing surface sensitivity. The principle behind the elastic Auger yield technique is the use of characteristic Auger electrons that have only been elastically scattered en route to escaping from the surface of the solid. In Fig. 4, shaded rectangles are used to show schematically the energy windows for electron emission after photoexcitation. The elastic Auger yield is collected using a fixed energy window centered on the Auger peak while the X-ray photon energy is varied during the SEXAFS measurement [22]. The electrons are typically collected using photoemission-type energy analyzers. It is apparent from Fig. 4 that when the X-ray photon energy is increased, the photoemission peaks will appear at higher energies in the spectrum, thus possibly interfering with the Auger peak. Therefore, before performing the experiment the core level binding energy and the characteristic Auger energy values for the absorbing atom must be used to assure at least a 300-eV spread at the absorption edge between the Auger peak chosen and the next photoemission peak on the lower energy side. The elastic Auger yield generally exhibits the best signal-to-background ratio characteristics and has the best surface sensitivity, because of limited sampling depth compared to radiative and nonradiative detection techniques. It also has the best discrimination capabilities against Bragg diffraction glitches because of the small acceptance angle of the detector, allowing it to be moved along the polar angle, relative to the sample normal and away from the directed peaks.

C. Partial Auger Yield

Most of the Auger electrons that leave the surface have suffered energy loss due to inelastic scattering. Because the inelastic scattering process is independent of the X-ray photon energy, the intensity of these electrons as a function of hν will also exhibit the EXAFS. The collection of inelastic and elastic Auger electrons leads to a decreased signal-to-background ratio, because the inelastic Auger electrons are spread over a wide energy range in which they constitute a smaller part of the total signal than the elastic Auger electrons do throughout the Auger peak. However, this is compensated for by an increased EXAFS signal and better ability to avoid interference with photoemission peaks. Obviously, surface sensitivity decreases for partial Auger yield (PAY) because the sampling depth is larger for inelastically scattered Auger electrons.

D. Total Electron Yield

As shown in Fig. 4, using total electron yield (TEY) implies collecting the high-energy primary photoelectrons and elastic Auger electrons, inelastic photoemission and Auger electrons, and secondary electrons. An inherent problem associated with this technique is that the photoelectron intensity is angular and energy dependent at any point in space [23]. It was first pointed out by Lee [9] that to have a direct relationship between the photoelectron intensity and the absorption coefficient, such as in Eq. 6, there has to be complete angular averaging of the photoemission signal. Martens et. al [18] also pointed out that the signal-to-background ratio depends on the incident beam angle; the optimal setting is 10°. Comparison of TEY and transmission EXAFS measurements has shown that although there is good agreement between the phases, the amplitude for TEY is generally <u>smaller</u> than for transmission. Comparison between TEY and elastic Auger yield (EAY) results shows similar effects: for example, Stohr et. al [22] report an amplitude for TEY reduced by 15% relative to EAY at approximately 250 eV above the Al K-edge for aluminum metal. The situation is still unresolved as results vary for different groups: Erbil et al. [24] obtained a 5%-10% amplitude reduction for TEY compared to transmission, for several different systems, while a more recent study made on gold metal and GaAs powders by Kemner et al. [25] revealed practically <u>identical</u> amplitudes for the two techniques. TEY is an especially easy technique to use, because collection of the electrons can be accomplished, in many cases, by simply suspending a biased metal plate over the grounded sample and measuring the drain current. TEY is an appropriate choice when it becomes impossible to avoid interference with photoemission peaks in the detector energy window. TEY is the worst of the electron detection techniques for surface sensitivity, Bragg diffraction glitches, and signal-to-background ratio.

E. Secondary Yield

Collection of secondary electrons involves using a narrow energy window very close to the vacuum level energy, because the energy for secondary electrons is typically 3-5 eV [23]. This way, it is possible to avoid the amplitude problems inherent in TEY, however, the signal for secondary yield is reduced.

F. Ion Desorption Yield

Our current understanding of electron stimulated desorption (ESD) of surface ions is that at least two mechanisms exist: in the Menzel-Gomer-Redhead (MGR) model [26], electronic scattering of valence electrons causes their ionization, resulting in repulsive ionic final states, while in the Knotek and Feibelman (KF) model [27], applied to strongly ionic systems, the ionization is due to core electron rather than valence electron excitation. In the KF model, desorption can occur as a result of intratomic Auger transitions for ionization of adatoms, or interatomic Auger transitions for ionization of substrate atoms. The Auger transitions involve valence electrons, some of which may be in bonding states, leading to the breaking of the adatom-substrate bonds. If the core electrons are photoionized, the intensity of the ions desorbed as a result of the KF mechanism will exhibit fine structure in direct relation to the EXAFS seen in the absorption coefficient. Jaeger et al. [28] reported the first SEXAFS study using ion desorption yield, in which O^+ ions were collected from a monolayer coverage of oxygen on Mo(100). Two complications severely limit using the ion desorption yield technique for SEXAFS studies. For many systems, particularly covalent ones, the MGR and possibly other mechanisms beside the KF process, contribute to the ion desorption yield but not to the EXAFS signal. The other limitation is that the ion yield SEXAFS signal is inherently weak.

IV. EXPERIMENTAL DETAILS

Our aim in this section is to provide a brief discussion of some of the more essential details of the experimental setup and data analysis. More details can be found elsewhere [1].

A. Experimental Setup

The most important components of the experimental setup are: the synchrotron radiation source, the monochromator, the incident beam and signal detection assembly, and the ultrahigh vacuum (UHV) sample chamber. Because the signal detected for SEXAFS is relatively weak, X-ray flux intensities of the order of at least 10^{10} photons/s are required. As a consequence, synchrotron radiation has played and continues to play an instrumental role in the development of the field. Because the acceptance angle of most electron energy analyzers is small, the X-ray beam requires focusing to approximately 1 mm^2 at the location of the sample. The energy resolution required is < 5 eV; however, 1-2 eV are more desirable, especially for details in the near edge region, and are often obtainable. Spectral purity of the X-ray beam is very important for a successful experiment. One source of particularly bothersome spectral impurity is due to harmonics, which are higher order reflections (the principal energy being the first order reflection) from the gratings or crystals in the monochromator. The three most effective ways to deal with harmonics are: (1) detuning monochromator crystals, that is, misorienting one crystal very slightly relative to the other [29], (2) using harmonic rejection mirrors, and (3) using filters.

Characterization of the surface using complimentary techniques such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and thermal desorption, ensures a more definitive study and, if performed prior to the SEXAFS study, may help in the optimization of the experiment. For example, identification of unwanted impurities on the surface and their removal may eliminate potential interference between spectra due to their overlap in energy or may enhance the sensitivity if the impurity atoms contribute significantly to the background.

The signal intensity is normalized by the incident beam intensity, which is typically monitored using the total electron yield produced in a coated metal grid intercepting the incoming beam. There are cases for which glitches due to Bragg peaks, harmonics, etc., are not removed by normalization sufficiently, and these features therefore remain in the spectra. This occurs when the response of the signal and reference monitors to the source of the glitches is not the same. Stohr et al. [30] suggested alternatively using the signal measured from a clean substrate as a reference signal and demonstrated the technique for 1/3 monolayer of oxygen on Ni(100).

B. Data Analysis

SEXAFS data are preferably analyzed by using the ratio method, and if that is not possible, one resorts to fitting the data in wavevector k space. The fine structure oscillations are isolated by first subtracting the pre-edge background from the reference-signal-normalized data, followed by subtraction of the atomic-like background above the edge and normalized with respect to the step height [14]. The dependence of the SEXAFS signal is converted from energy to a wavevector in this process. The isolated data are then Fourier transformed from k space to R space. The Fourier transform generally looks like a multipeaked profile, in which each resolved peak corresponds to shell distributions of neighboring atoms surrounding the absorbing atom. If the individual peaks are well resolved with respect to one another, then another Fourier transform is performed, back to k space, over the region isolating a particular peak. Thus, fine structure oscillations due to a particular shell are isolated in this way. Performing a ratio between the isolated-shell sample data and similarly obtained model compound data can provide relative amplitude and phase results. Otherwise, if the peaks are not well resolved, one has to resort to a multishell fitting of the data.

V. APPLICATIONS TO SURFACE PROBLEMS

A. Gas-Solid Reactions

Most of the gas-solid systems studied using SEXAFS involve molecules of gas that dissociate on reaction with the surface and become chemisorbed, typically in ordered overlayer arrangements determined by the symmetry of the surface. Compound formation at the surface is also possible, as for example, oxide formation at metal and semiconductor surfaces. The presentation in this section is chronological, by system studied, with greater emphasis placed on studies completed after the publication of reviews by Stohr [1] and Citrin [2].

1. Gas-Metal Reactions

I/Ag(111). This is the very first system to be studied using SEXAFS, demonstrating the power of the technique for surface structure determinations. The studies of the system with 1/3 monolayer (ML) ($\sqrt{3}$x$\sqrt{3}$)R30° iodine on Ag(111) by Citrin et al. [31,32] basically verified the structure determination using LEED but with much more precision. The data were obtained at the I L_3-edge, using the EAY technique. The I-Ag bond length was determined to be 2.87±0.03 Å (compared with 2.80±0.15 Å for LEED determined by Forstmann et al. [33]) using γ-AgI as a model compound. The effective coordination number was deduced using Eq. 4 according to which the chemisorption site was determined to be in the threefold hollow configuration.

I/Cu(100) and Cu(111). Citrin et al. [34] also investigated the local structure of iodine on Cu(100) and Cu(111) using TEY SEXAFS measured at the I L_3-edge. The polarization dependence of the EXAFS signal was fully exploited to make an unambiguous determination of the chemisorption site for both cases. LEED spot patterns revealed 1/3 ML $(\sqrt{3}\mathrm{x}\sqrt{3})$R30° iodine on Cu(111) and 1/4 ML p(2x2) iodine on Cu(100). Using the ratio method and γ-CuI as the standard, the iodine on Cu(111) was found to have a bond distance of 2.66±0.02 Å, and the iodine on Cu(100) had a bond distance of 2.69±0.02 Å. The smaller error bar for this study relative to the authors' I/Ag(111) study was attributed to improved data quality using TEY rather than EAY. The authors showed in a convincing fashion, from analysis of the polarization-dependent isolated EXAFS amplitudes, that chemisorbed iodine sets in a threefold hollow site on the Cu(111) surface and in a fourfold hollow site on the Cu(100) surface. Additionally, they showed that EXAFS amplitudes may be transferred between bulk and surface systems within at least 25%.

I/Ni(100). The TEY SEXAFS study by Jones et al. [35] of the 1-2 ML surface iodide phase formed on a Ni(100) surface is significant because they were the first to apply the fitting approach to data analysis. Using NiI_2 for a standard, they used both the conventional method of isolating the first shell contribution to the signal and performing a ratio and a curve fitting method, for which the calculated phase shifts are adjusted by first fitting NiI_2 data. Jones et al. found excellent agreement for the results obtained using the two methods. However, a more recent study by the same group [36] showed that, in fact, the first and second shells in the Fourier transform are not separable, thus excluding the ratio method in this case as viable. In this study, the authors were able to show, for the 1/2 ML c(2x2)I on Ni(100) structure, that the fitting method can be used successfully to determine the local structure. They found the I-Ni bond length to be practically unchanged relative to the value for the bulk of NiI_2 (2.78±0.02 Å), and the absorption is at the fourfold hollow site.

O/Al(111). Both Johansson and Stohr [37] and Bachrach et al. [38] performed SEXAFS studies, using TEY and measured at the O K-edge, on the ~ 1 ML(1x1) O on Al(111) structure and obtained differing results. The O-Al near neighbor distance quoted by Johansson and Stohr was 1.79±0.05 Å while Bachrach et al. obtained a value of 1.92±0.05 Å. Although polarization-dependent SEXAFS data were obtained, the threefold hollow chemisorption site could not be confirmed as deduced from previous LEED studies [39]. A reexamination of previous LEED data was prompted because the atomic distances obtained using SEXAFS varied significantly from those obtained from LEED. The large error bars can in part be attributed to a significantly oxidized aluminum underlayer contributing to the signal.

O/Ni(100). SEXAFS studies by Stohr et al. [30] on this system helped contribute to understanding oxygen chemisorption on nickel surfaces. The O K-edge was measured in the PAY mode, and the polarization dependence of the signal was exploited by collecting data for 10° and 90° incidence angles. The study was stimulated by predictions made from generalized valence bond electronic structure calculations [40] claiming that the p(2x2) and c(2x2) structures with O in the fourfold hollow site should have considerably different displacements when measured along the surface normal. Using NiO for the standard, unambiguous evidence for the fourfold hollow site for O was given in the c(2x2) structure, with a bond length equal to 1.96±0.03 Å, and no evidence was seen from a theoretical model of different displacements for the two structures mentioned above.

O/Ni(110). The SEXAFS study of this system by Baberschke et al. [41] was, in execution, very similar to the study by Stohr et al. [30], but it yielded unprecedented precision in structure determination. The long bridge site of the ~ 1/3 ML O(2x1) on Ni(110) structure was identified having the O-Ni near neighbor distance of 1.85±0.02 Å. Due to the precision, the oxygen-induced reconstruction of the Ni(100) surface was determined to be of the "sawtooth" type, while eliminating the possibility for the buckled-surface, based on the absence of the third shell peak in the Fourier transform of the EXAFS data. The "sawtooth" reconstructed surface was established based on the intensity of the <u>fourth</u> shell peak and the polarization dependence of the data [42].

O/Cu(110). This system, studied by Dobler et al. [43,44] is very similar to the O/Ni(110) system that was studied later. The investigation was carried out in much the same way as for the O/Ni(110) system discussed above and had similar precision. The twofold bridge site of the ~ 1/2 ML O(2x1) on Cu(110) structure was identified, with an O-Cu bond length of 1.84±0.02 Å, using the relative amplitudes of the first and second neighbor shell data. This low-symmetry site had been a source of controversy, because metals were usually found to have high symmetry sites. It was suggested by Dobler et al., based on the evidence of the absence of the third shell peak and presence of the fourth shell peak in the Fourier transform, that the Cu(100) exhibited O-induced "missing-row" reconstruction. Their later studies [41,42] on O/Ni(110) confirmed this. However, a possible explanation for the different reconstruction for the two systems may be due to stronger O/Ni than O/Cu chemisorption [42].

O/Cu(111). Polarization-dependent SEXAFS studies above the O K-edge were performed on this system by Haase and Kuhr [45] using PAY. For ~ 1/2 ML O on Cu(111), they found evidence for a reconstructed and oxidized surface; the reconstruction was evident in the increased Cu-Cu distance on the surface compared to bulk. The system is known to exhibit a disordered surface. The relative amplitudes at different incident angles are used to identify the threefold hollow site for O (R_1 = 1.83±0.02 Å) close to the surface. The authors could not determine if the O was above or below the surface Cu atoms.

O/Ag(110). This system was found to be very similar to the O/Cu(110) system. Two sets of studies have been performed on O/Ag(110), both in a very similar fashion to the studies on O/Cu(110) and O/Ni(110) discussed above. Puschmann and Haase [46] identified the twofold bridge site of the O(2x1) on Ag(110) structure but were unable to establish the type of reconstruction due to reduced data quality. Recently, Becker et al. [47] were able to identify the reconstruction as the "missing-row" type, as in O/Cu(110), and to confirm the surface structure. The first neighbor distance of O is quoted as 2.04±0.03 Å and the second neighbor distance as 2.19±0.03 Å.

S/Ni(100). The first study performed on this system was by Brennan et al. [48]; this system was chosen because it was one of the best known systems at the time. The measurements were made in the EAY mode, at the S K-edge, for different angles of incidence. The high quality signal-to-noise ratio allowed, for the first time, a determination of the fourfold hollow site of the ~ 1/2 ML c(2x2)S on Ni(100) structure from the combination of the determined first and second neighbor distances without the relative amplitude analysis. The S-Ni bond length was determined to be 2.23±0.02 Å. Thiophene (C_4H_4S) chemisorption on Ni(100) was later studied by Stohr et al. [20], with varying S coverages, for which the molecule was found to dissociate on a clean surface at temperatures as low as 100 K to the c(2x2)S on Ni(100) structure. Thiophene was found intact for an experiment performed with an oxygen-predosed Ni(100) surface.

S/Ni(111). The model proposed for the local structure of S on Ni(111) by Kitajima et al. [49] is presently somewhat in question. Based on their relative amplitudes for the polarization-dependent first shell data, Kitajima et al. proposed that, for the ($5\sqrt{3}$x2)S on Ni(111), drastic surface reconstruction into a pseudo-c(2x2)S on Ni(100) results from sulfur adsorbed on the pseudo-fourfold hollow site. Ohta [50] performed X-ray standing wave experiments on the same system and determined that the results for the two experiments cannot be reconciled if one assumes a standard type of site occupation for sulfur on Ni(111). However, if one assumes a reconstructed surface as proposed by Kitajima et al. and an outward expansion of the surface by 0.15 Å, then the results agree.

S/Cu(111), (100), and (110). Prince et al. [51] have performed a SEXAFS and X-ray standing wave study of the S/Cu(111) system. LEED patterns revealed a $(\sqrt{7}x\sqrt{7})$R19° S on Cu(111) structure after exposure of a clean Cu(111) surface to H_2S in excess of 5 L. The SEXAFS data were collected for two angles of incidence using the EAY technique. This study suffers from a lack of precision (R_1 = 2.30±0.1 Å) due to the high level of noise and because the fitting method was chosen for data analysis. Although the exact structure of the surface was not determined, the authors were able to infer from their results that S lies both below and above the Cu atoms. The S atoms below the Cu layer occupy sixfold hollow sites, while the Cu are in identical off-bridge (towards atop) sites, and the S atoms above are in atop sites. In a study performed on the S/Cu(100) system, however, Kitajima et al. [52] were able to determine, using polarization-dependent SEXAFS results, the surface structure as $(\sqrt{7}x\sqrt{7})$R14°. Measurements were collected, at three incident angles, in the fluorescence yield mode, and surface coverage was estimated to be ~ 1/2 ML. The S-Cu bond length was 2.33±0.03 Å. Using the combined results from the SEXAFS and LEED measurements, Kitajima et al. proposed a model for surface reconstruction involving clockwise and counterclockwise rotational displacements of Cu atoms relative to the S adatoms of 0.59 Å.

Recently, Atrei and coworkers [53] conducted a SEXAFS study of sulfur adsorption on Cu(110). Polarization-dependent measurements were taken using the EAY technique at varying S coverage. In conjunction with LEED results, the authors reported a c(2x2) surface structure at low S coverage, while ruling out reconstruction or multiple adsorption sites at higher coverage in favor of an expansion of the first Cu interlayer distance. The S atom was found to occupy the twofold hollow site, with the Cu-S bond length of 2.37±0.03 Å, throughout the coverage range studied.

Cl/Cu(100) and Ag(100). The study of this system by Citrin et al. [54] was stimulated by conflicting results for the c(2x2) Cl on Ag(100) structure from LEED measurements and from comparison of calculated and measured photoemission spectra. Copper was chosen because its photoemission peaks did not interfere with the EAY signal. The adsorption site was identified as the fourfold hollow site of the c(2x2)Cl on a Ag(100) structure with a Cl-Cu bond length of 2.37±0.02 Å. The polarization-dependent SEXAFS data showed an anisotropy in the higher shells due to an averaging of four third-nearest-neighbor atoms in the second layer and eight fourth-nearest-neighbor atoms in the first layer. The structural parameters obtained from the Citrin et al. study were used to calculate the photoemission spectra for Cl/Cu(100) and were found to have excellent agreement with experimentally measured spectra. In this way, the importance of providing experimentally-deduced structural results was established. Although difficult, studies have been carried out on the Cl/Ag(100) system [55]. The system had to be studied in TEY mode, due to photoemission peak interference for EAY detection, and at 100 K, due to anharmonic distortions of the SEXAFS spectra being greater at room temperature. Coverages of 2/3 and 1/3 ML of Cl were studied: a weak LEED pattern consistent with the $(\sqrt{3}x\sqrt{3})$R30° structure was observed for 2/3 ML Cl coverage, while no LEED pattern was observed for the 1/3 ML coverage. Fitting of the data was used to obtain distances, and a threefold hollow absorption site was proposed for both coverages but not identified due to insufficient polarization-dependent data.

Te/Cu(111) and Cu(100). Comin et al. [56] made a SEXAFS study of both systems using TEY and AEY techniques. They identified the 1/4 ML p(2x2)Te on Cu(100) structure (nearest neighbor distance R_1 = 2.62±0.04 Å) and the 1/3 ML $(2\sqrt{3}x\sqrt{3})$R30° Te on Cu(111) structure (R_1 = 2.69±0.06 Å), the latter having a novel sixfold quasisubstitutional site for which Te substitutes for Cu in the surface layer. The complete understanding of the nature of chemisorption for the low symmetry site is of interest in view of the experimental findings. The fact that Te has a relatively large atomic size and low reactivity is thought to play a role.

Xe/Cu(111). A temperature-dependent SEXAFS study on this system [57] has recently been reported. The authors revealed that at 77 K, the Xe adatoms form a commensurate $(\sqrt{3}x\sqrt{3})$R30° structure, in which the Xe atom sets in the threefold hollow site, while between 18 and 47 K, they form an incommensurate structure because the Xe-Xe spacing is different than the distance between threefold hollow sites on the Cu(111) surface.

2. Gas-Semiconductor Reactions

Gas-semiconductor reaction systems are generally more complex and not as well understood as gas-metal systems. Early studies of oxygen chemisorption on GaAs(110) [58] and Si(111)2x1 [59] helped establish PAY as a viable technique but gave inconclusive results due to the low quality of the data. The first substantially quantitative study [60] of this nature was conducted on the Te and I on Si(111)7x7 and Ge(111)2x8. For about 1 ML coverage and data collected using the TEY mode, I on both surfaces was found to occupy the onefold atop site, while the twofold bridge site was identified for Te/Si(111) and the threefold h.c.p. hollow site for Te/Ge(111). The I/Si(111), I/Ge(111), and Te/Si(111) results fit the pattern for which either the monovalent I or divalent Te uses up the dangling bonds and thus prevents the surface from undergoing reconstruction while Te/Ge(111) does not. A later study [61] of Te/Si(111) was motivated by the desire to determine how the unusual Te twofold bridge site occupation changed as a function of surface coverage. For about 1/4 ML coverage, the authors reported a 100Si(111) ($\sqrt{3}$x$\sqrt{3}$)R30°-Te structure. The Te atoms were determined to reside in the twofold bridge site again, but the first- and second-neighbor distances were found to be longer than those for ~ 1 ML coverage. A possible explanation offered for the distance lengthening was a slight tilting of the Te atoms relative to the surface. The Cl/Si(111) and Ge(111) systems were studied in a separate work, showing that Cl occupied the onefold atop site on annealed Si(111)7x7, annealed Ge(111)2x8, and quenched Si(111)($\sqrt{19}$x$\sqrt{19}$) surfaces. These data agreed with the chemisorption geometry inferred from earlier photoemission results for the Si(111) surface but not for the Ge(111) surface. In a recent SEXAFS study [62] made on the Si(111)7x7-Cl system, using the ion desorption technique, results were reported that which are in very good agreement with the previous study made using EAY. The Cl-Si bond length was determined to be 2.00±0.02 Å.

The first reliable study [65] of oxygen on a Si substrate was done on Si(100). Polarization-dependent O K-edge spectra were collected in the TEY mode for ~ 1 ML coverage of O on Si(100). It was determined from LEED that at 1 ML coverage, the (2x1) reconstruction at the surface was lost. The authors found evidence for two types of bridge site occupations: between Si atoms in the first layer and between Si atoms in the other topmost layers. The O-Si bond length was found to be 1.65 Å, and the Si-O-Si bond angle was ~ 120°.

3. Molecule-Solid Reactions

The first application of SEXAFS to the study of chemisorbed molecules was made on the formate (HOCO) on Cu(100) system [66]. The data was collected using the PAY mode above the O K-edge. Formate is a planar molecule, which in this study was determined to be positioned on the Cu(100) surface so that the O atoms nearly occupied the fourfold hollow sites, with the molecular plane straddling the Cu-Cu bridge site. This determination was challenged, however, in a later study [67], in which it was shown that the molecule occupied the "diagonal-atop" site where the C atom is situated directly over the Cu atom and the molecular plane is positioned along the diagonal of two Cu(100) squares. The site assignment was similar for the Cu(110) surface, but in this case, the molecular plane was aligned with the ridge of contiguous Cu surface atoms [68]. It was suggested by Crapper and coworkers that the error in the first study could be attributed to improper Fourier filtering of the data so that insufficient isolation of first and second shell data was carried out. A recent study [69] using photoelectron diffraction and reassessment of previous results showed that the site occupancy of formate on both Cu(100) and Cu(110) is nearly identical and of the "aligned-bridge" type in which the O atoms are in the atop positions. The Cu-O bond length was 1.98±0.04 Å.

B. Liquid-Solid Reactions

Although limited in quantity, EXAFS studies of liquid-solid reactions at surfaces have shown some of the possibilities in this and related subject areas. Most studies in this subject area have dealt with aqueous metal sorption on oxides. One of the earliest such studies involved Co K-edge fluorescence yield EXAFS measurements of $Co(NO_3)_2$ solutions on reaction with γ-Al_2O_3 and TiO_2 surfaces [70] to test how different oxides may affect the sorption process. The sample was prepared by exposing the surface of the oxides to a modified solution of $Co(NO_3)_2$, adjusted so that pH values selected would prevent precipitation, followed by centrifuging the samples on equilibration to remove excess solution. The experiment was performed at atmospheric pressure in closed vials to prevent loss of liquid. Coverage was estimated to be ~ 0.1 ML for Co^{2+} ions. The authors were able to determine that Co was in fact adsorbed on the surface and not in precipitate form. EXAFS results indicated formation of multinuclear Co complexes on the oxides: on γ-Al_2O_3, each Co was found to have six O at 2.08 Å in the first shell, four Co at 3.12 Å in the second shell, one Al third neighbor at 3.20 Å, and a distant Co neighbor at 6.1 Å. On TiO_2, each Co was determined to have about one Co (at 3.36 Å) and one Ti (at 3.31 Å) in the second shell and no distant neighbors. The conclusion reached was that Co was bonded to the surfaces of the oxides without significant precipitation of Co-hydroxide or diffusion of Co into the oxides. The difference in the local structure of Co adsorbed on the surfaces was interpreted to mean that γ-Al_2O_3 promoted formation of greater polymerized Co complexes on its surface than of TiO_2 on its surface. A more recent study of Co complexes formed on γ-Al_2O_3 surfaces as a function of sorption density [71] showed that as the sorption density decreases, highly polymerized Co complexes become less important in favor of monomeric species. A similar study was carried out on Pb complexes formed on γ-Al_2O_3 [72] for which the Pb atom was determined to have one O at 2.23 Å and two at 2.46 Å in the disordered first shell, and one Pb at 3.55 Å and one Al at 3.77 Å in the second shell, suggesting that the reaction on the aluminum oxide surface resulted in the formation of inner-sphere Pb complexes that are less polymerized than Co complexes on the same surface.

C. Solid-Solid Interfaces

Solid-solid interfaces involve some of the most interesting and complicated problems studied using SEXAFS, many having direct relevance to technological problems facing us today. Examples include Schottky barrier formation, clustering, epitaxial growth, compound formation, and solid solution formation. This area of study is divided into three subsections: metal-metal, metal-semiconductor, and semiconductor-semiconductor interfaces.

1. Metal-Metal Interfaces

One of the earliest studies on metal-metal interfaces was on the Co on Cu(111) system [73]. The system was studied for ~ 1 ML and ~ 1/3 ML Co evaporated on Cu(111). The polarization-dependent SEXAFS results were used to determine that at 1 ML coverage, a two-dimensional monolayer of Co was formed with each Co atom having 6 nearest neighbors at the same distances as in bulk Co. The Co-Cu distance was reported to be 0.04 Å shorter than the Co-Co distance. It was determined that small, three-dimensional Co clusters formed at 1/3 ML coverage. The coordination number was ~ 3 for Co in this case, with distances the same as those for bulk Co. This study demonstrated that the extent to which a surface undergoes wetting is a direct function of coverage. A glancing-angle fluorescence EXAFS study on a 0.01 ML coverage of Hf on a Pt/C multilayer [74] (with Hf covered by 10 Å of amorphous carbon) demonstrated in dramatic fashion the level of sensitivity of the technique. In a recent in situ study of a

ML coverage of Cu on polycrystalline Pt [75], important to the understanding of electroplating and corrosion, the authors collected glancing-angle fluorescence EXAFS data with the sample in the presence of an electrolyte and an applied voltage. Tentative results suggested up to 4 oxygen atoms at ~ 1.98 Å in the first shell with the type of second shell atoms undetermined.

2. Metal-Semiconductor Interfaces

One of the first studies of its kind, the SEXAFS study of Ag on Si(111)7x7 [76] was performed for several coverages. The authors reported that at 1 ML and greater coverage, coexistence of the ordered and disordered phases occur. However, measurements collected for 0.6 ML coverage indicate a uniform ordered phase so that complications due to Ag clustering were eliminated. A $(\sqrt{3}x\sqrt{3})$Ag/Si(111) surface structure was reported with the Ag atoms located in the interstitial adsorption site. An anisotropy was determined in the Ag-Si distance, at 2.48±0.04 Å along the surface normal and 2.46±0.04 Å at 65° relative to the surface normal. SEXAFS has also been used to study the Pt/Si(111)7x7 system [77], for which it was also reported (for 0.8 ML coverage) that the metal atom was located in the sixfold interstitial lying midway between the top and second Si layers. Careful consideration of their results allowed the authors to make a determination of the relaxation of the Si atoms surrounding the Pt atoms in response to the interstitial site occupation. It was reported that the top Si layer was lifted by 0.58 Å and that the six Si atoms moved 0.15 Å outward from the Pt atom. Increasing the Pt coverage was reported to promote intermixing in the top two Si layers, followed by, most likely, nucleation of Pt_2Si coordinated clusters. The authors in a recent study of the Cs/Si(111)7x7 system [78] attempted to determine the nature of bonding of the adsorbed atom as a function of coverage, ranging from 0.4 ML to greater than 1 ML. The nature of bonding at 1 ML coverage is inferred to be covalent and at 0.4 ML is inferred to be ionic, due to an increase in bond length at lower coverage. There have also been several recent studies of Sb on Si surfaces: the Si(100)2x1-Sb system studied by Richter and coworkers [79] and the Sb on Si(111) system studied by Woicik et al. [80] In the first study, SEXAFS and STM were used to determine that Sb occupied a modified bridge site having the Sb-Sb near-neighbor distance of 2.88±0.03 Å. Each Sb atom is bonded to two Si atoms with a bond length equal to 2.63±0.04 Å. In the second study, it was determined using SEXAFS in conjunction with X-ray standing wave measurements that Sb atoms occupy threefold atop sites where each Sb atom is bonded to one Si atom. The X-ray standing wave results indicated that Sb atoms reside 2.53±0.1 Å above the Si top layer in clear support of the pyramidal occupation site model.

3. Semiconductor-Semiconductor Interfaces

Local structure studies of semiconductor-semiconductor interfaces have obvious technological importance in device applications. Understanding the role of strain and adatom-adatom and adatom-substrate chemical interactions on the determination of structure at the interface is of great interest. There have been several studies made on the Ge/Si interface system. In an earlier work, SEXAFS and other surface techniques were used to study the onset of epitaxy of the Si/Ge(111) system [81]. A thin Si film (~ 5 Å) was grown by solid phase epitaxy on Ge(111) at room temperature. SEXAFS spectra were measured, using EAY, as the sample was annealed from 370°C to 800°C. The Si-Si first shell distance was found to increase from 2.35 Å (at room temperature) to 2.44 Å (at 800°C), the same as the Ge-Ge distance, indicating strained Si-Ge bonding. The degree of intermixing (monitored from the Si-Ge signal) increased with annealing temperature. A faint 1x1 LEED pattern was observed after the 800°C anneal, indicating that a pseudomorphic Si-Ge alloy had formed that had a lattice constant of bulk Ge [82]. In a related study, Comin et al. [83] determined the interface local structure of ~ 1 ML of Ge on Si(111)7x7 using SEXAFS. The Ge atoms were determined to adsorb in the atop site and bond together to form chains running parallel to the surface; these chains were bridged together with similar Si chains to terminate the structure. The Ge-Si bond was strongly compressed to 2.38±0.02 Å, while the Ge-Ge bond was found to be unchanged from the bulk value.

D. Buried Interfaces

One of the best applications of the total reflection EXAFS has been for studying buried interfaces. The idea behind total reflection EXAFS is simple enough: the angle of incidence is kept below the critical angle for the substrate layer so that most of the X-ray radiation is reflected off the interface and a small portion penetrates the substrate layer (typically < 30 Å). The first detailed measurements using total reflection EXAFS were carried out by Martens and Rabe [84] for the K-edge of a copper metal thin film. The authors pointed out that total reflection EXAFS is generally not directly proportional to the absorption EXAFS because of a phase and amplitude contribution from the real part of the refractive index to the signal, whereas the absorption EXAFS is only proportional to the imaginary part. This was deemed to be a severe drawback for the technique; however, Heald and coworkers [85] demonstrated that, in conjunction with X-ray reflectivity as a function of incident angle data, a simple analytic correction scheme can be used to make determinative studies of interfaces using total reflection EXAFS. The correction involves isolating the real and imaginary part contributions to the collected spectra and normalizing out the real part. For this study Heald et al. chose the Al/Cu bilayer system and reported that the interface was made up of a thin region containing interdiffused Cu and Al and a $CuAl_2$ alloyed phase. Total reflection EXAFS was used to study the GaN/GaAs(111) interface [86], formed after passivating GaAs with 200 Å of Si_3N_4. The authors found that the Ga-N bond lengths at the interface were larger (2.2 Å) than those for bulk GaN (1.94 Å). Fourier transforms of their data revealed negligible mixing of GaAs and GaN. Tan et al. have made an interesting study of ion-beam induced reactions at the Al/Nb buried interface [87]. The ion-beam mixing was accomplished with bombardment by 50 keV Al^+ ions on the sputtered Al/Nb sample. Results revealed that the interface was rougher as a result of the ion-beam mixing and that compound formation and interatomic diffusion were small. Two separable regions were identified at the interface: a Nb rich layer, having at least short-range order, is immediately below the Al layer and a relatively disordered Al rich layer is just below the Nb-rich layer. The influence of annealing on the Ni/C interface, for Ni-C multilayers, were recently studied using total reflection EXAFS [88]. Annealing at 450°C resulted in the crystallization of the Ni layers from the amorphous phase, as deduced from the identification of four Ni shells (at 2.45 Å, 3.42 Å, 4.25 Å, and 4.9 Å) similar to those of polycrystalline Ni foil. The Ni-C bond length was reported at 1.92 Å. Evidence from X-ray reflectivity was seen for increased interface roughness at high temperatures, inferred to be due to rearrangement of atoms at the interface and not to interdiffusion.

VI. FUTURE PERSPECTIVE

One drawback to SEXAFS studies has been the relatively low signal-to-noise ratio due to the small area of surface exposure and the selection of signal collected. Just as the first generation of dedicated synchrotron facilities played an important role in establishing SEXAFS as a viable surface technique, the second generation will be instrumental in bringing improvements in the quality of its data. For example, the Advanced Photon Source being built at Argonne National Laboratory will provide a synchrotron radiation flux several orders of magnitude greater (for a small diameter beam suitable for surface studies) than existing facilities can currently provide. The increase in flux will also enable time-resolved studies, which are of great interest for studies involving reactions at surfaces, relaxation and reconstruction processes, and interdiffusion of atoms over time scales presently incompatible with data collection times.

Recently, the trend in SEXAFS research has been to study more complicated surface problems as our understanding of surfaces increases. Advances in instrumentation, measurement techniques, and analysis methods have also contributed to this trend. In particular, the theoretical work being done to advance the understanding of the EXAFS process has excellent potential in providing a method of fitting data in r-space that could simplify and shorten data analysis considerably.

A relatively unexplored area of research related to surface science has been the study of buried interfaces using total reflection EXAFS. A bothersome complication involving crystalline systems are the Bragg peaks that complicate the data. As improvements are made in ways to circumvent the problem, this subject area should attract more interest because of its natural applicability to many technologically related topics.

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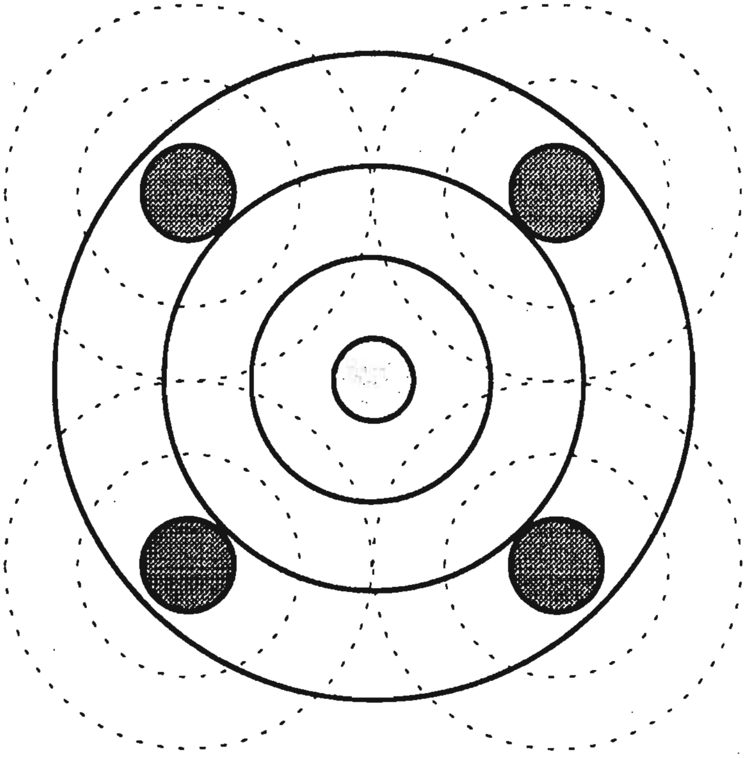

Figure 1. Illustration of outgoing photoelectron wave (solid line) and the portion of the wave scattered from the surrounding atoms (dashed line).

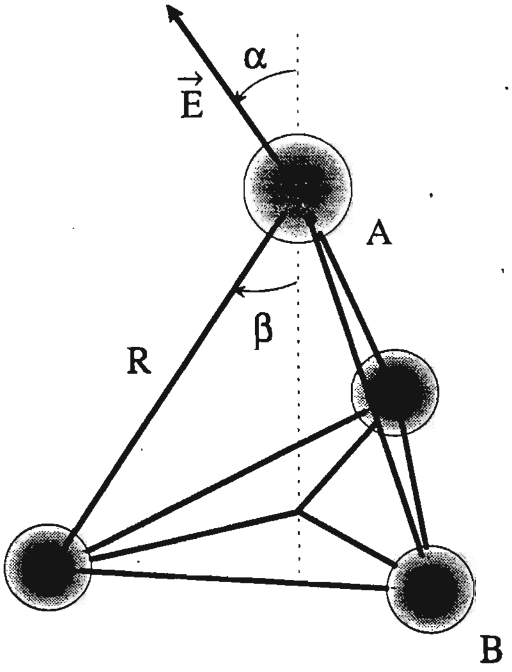

Figure 2. Schematic of adatom A in a three-fold hollow site configuration with substrate atoms B. **E** is the X-ray electric field vector, R is the near neighbor distance, and α and ß are the angles made by **E** and $\mathbf{R}_{Aj}$ relative to the surface normal, respectively.

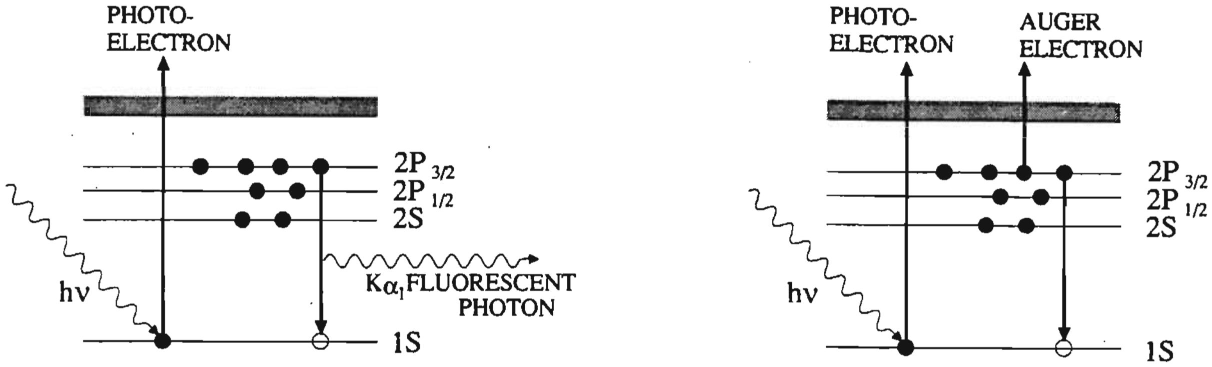

Figure 3. Schematic of the photoemission of a K shell core electron due to the absorption of an X-ray photon and the annihilation of the resulting core hole by two mechanisms: (a) K_α fluorescence and (b) Auger electron emission.

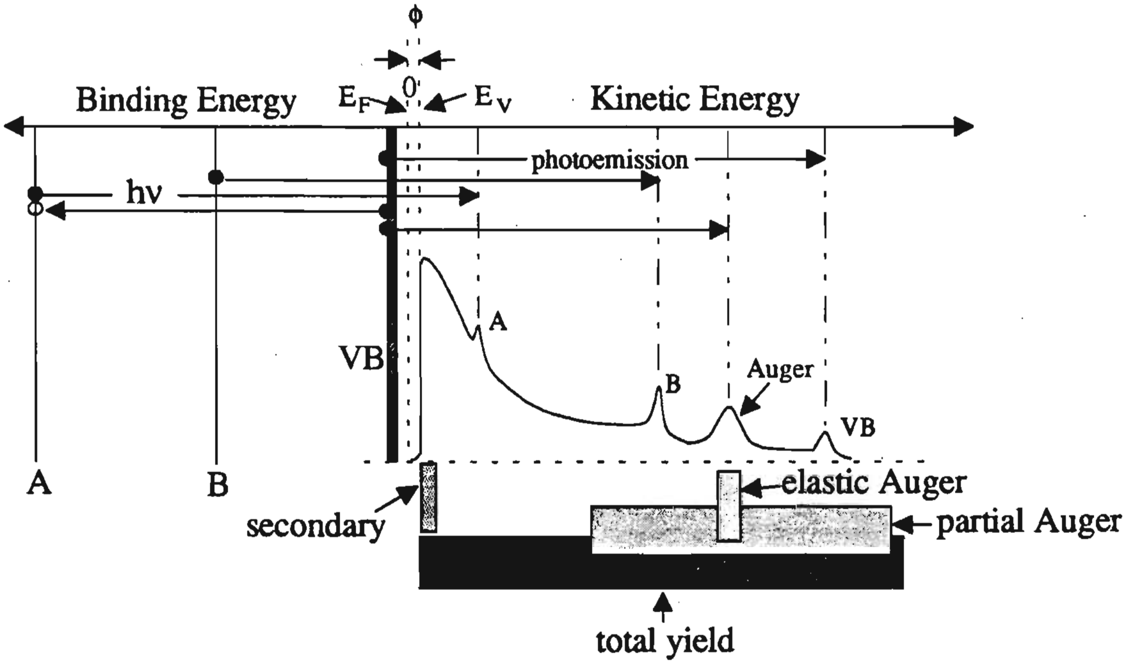

Figure 4. Schematic showing the photoemission spectra and a simplified three-level system associated with the profile. An electron is photoemitted from core level A, B, or the valence band (VB) after the absorption of an X-ray photon with energy hν. The energy zero is chosen at the Fermi level (E_F), which is separated from the vacuum level (E_V) by the work function ϕ. The energy window settings used with the various detection modes are shown below the photoemission spectra. Adapted from Reference 1.

8. HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPIC CHARACTERIZATION OF INSULATORS FOR Si TECHNOLOGY

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ABSTRACT

High resolution electron energy loss spectroscopy (HREELS) in conjunction with a number of other surface analytical techniques has been applied to study semiconductor and insulator surfaces and interfaces of technological importance. Results are presented for HREELS applied to characterize single-crystalline SiO_2 surfaces, CaF_2/Si(111) interfaces, as well as thin-film SiO_2/Si(100) grown in situ by thermal oxidation or by chemical vapor deposition. Interface phonons can be identified for thin epitaxial insulator films and thin film properties (dielectric function) can be obtained for thin amorphous films. The mechanisms of hydrocarbon removal from Si wafers by HF and ultraviolet-ozone cleaning, processes crucial for Si technology, are revealed.

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9. SURFACE MODIFICATION TECHNIQUES: A SUMMARY REPORT

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I. INTRODUCTION

Surface modification of materials is of tremendous significance in a legion of technological applications. As a matter of fact, surface modification offers the best of both worlds: one can modify the surface to attain desired surface characteristics without altering the bulk properties. Both inorganic (metals, ceramics, glass) and organic (polymeric) materials are modified for many and varied reasons or purposes (decorative, functional, protective), and a large number of techniques exist to modify surfaces. The choice of the proper technique for surface modification in a given situation depends on a host of reasons, e.g., nature of substrate material, intended purpose of surface modification, and economic considerations.

This Summary Report covers the following: various reasons for modifying both inorganic and organic surfaces, general surface modification techniques, separate catalogs of modification techniques specific or suitable to inorganic and organic materials, and research needs.

The field of surface modification is very dynamic and vibrant; much has been accomplished, but much more needs to be done and understood.

II. INORGANIC (METALS, CERAMICS, GLASS) SURFACES MAY BE MODIFIED TO

- Make them more adhesionable
- Increase their adhesion durability
- Improve tribological behavior
- Improve corrosion resistance
- Reduce degradation due to environment
- Improve mechanical properties
- Alter surface electrical characteristics.

III. POLYMER SURFACES MAY BE MODIFIED TO

- Make polymer surfaces more adhesionable
- Increase their printability
- Make polymer surfaces more wettable
- Make polymer surfaces hydrophobic (low energy, less wettable, nonsticky)
- Provide an enclosing layer
- Improve tribological behavior
- Prepare polymer surfaces for metal plating
- Provide enzyme immobilization
- Provide flame resistance
- Provide luster
- Provide antistatic properties
- Control permeation/diffusion

- Alter surface conductivity
- Improve abrasion/scratch resistance
- Reduce electrostatic charging problem
- Control surface electrical characteristics
- Alter optical characteristics
- Reduce/prevent degradation by deleterious environment.

IV. SURFACE MODIFICATION TECHNIQUES ARE USED FOR

Inorganic Materials (metals, alloys, ceramics, glass) and organic materials (polymers).

A. Broad Approaches to Surface Modification

The objective is to obtain a surface with desirable topography, chemical moieties, or mechanical/metallurgical characteristics.

1. Chemical

- Creation of new surface chemical groups (surface restricted, deep)
- Deposition of a discrete layer (coupling agent, grafting, Langmuir-Blodgett [LB] film, metal layer)
- Removal of some surface material (contamination, plasticizers, additives).

2. Physical

3. Mechanical

4. Metallurgical

Note: The surface modification techniques can also be broadly classified into two categories: wet and dry.

B. General Surface Modification Techniques

- Chemical
- Physical
- Mechanical
- Metallurgical
- Microbial
- Vacuum evaporation (removal of low molecular weight [mol. wt.] materials)
- Pressure (removal of weak boundary layers)

1. Chemical Surface Modification

- Chemical reactions (oxidation, sulfonation, ozonation, phosphatization, chromate conversion, amination, . . .)
- Grafting
- Selective etching
- Deposition of LB monolayers
- Deposition of coupling agents, e.g., silanes (also silane deposition followed by plasma treatment)
- Surfactant adsorption

- Photochemical, using proper photoactive compounds
- Solvent (surface swelling)
- Dissolution (proper second phase in contact, which can dissolve undesirable low mol. wt. materials)
- Prevention of diffusion of low mol. wt. materials to the surface
- Electroless metal deposition.

2. Physical Surface Modification

- Plasma
  - Radio frequency (RF)
  - Microwave
- Corona
- Flame
- Ultraviolet (UV)
- UV sensitized
- Ozone
- UV/Ozone
- X-ray
- Laser
- Electron
- Ion bombardment
- Ion implantation
- Ion plating
- Thin metal layer deposition
- . . .

3. Mechanical Surface Modification

- Blasting or abrasion in air
- Surface texturing (lithographic technique)
- SABRA (Surface Activation Beneath Reactive Adhesive)
- Casting against other materials (e.g., polymers against Pt, Hg)
- Rubbing against other materials.

4. Metallurgical Surface Modification

Metallurgical techniques include those that modify the mechanical (tribological, abrasion) or corrosion characteristics.

- Ion implantation
- Ion plating
- Cladding
- Laser
- . . .

V. RESEARCH NEEDS

A. Organic (Polymeric) Surfaces

- Cross-compare various modification techniques (plasma, corona, flame, etc.).
- Understand the deactivation of the treated surface, both mechanistic and kinetic aspects.
- Explore further the laser surface modification technique.
- Understand the mechanism of photochemical modification approach.
- Investigate the relative chemical versus mechanical contributions to adhesion to polymer surfaces.
- Characterize acid-base relationships by two or three different techniques and cross-compare; also, compile a comprehensive data base relative to acid-base characteristics.
- Explore in detail the relation between acid-base functionalities on the surface and their adhesion to a variety of overcoats, including metals.
- Understand the mechanism of silanes as adhesion promoters on polymeric surfaces. Also, other adhesion promoters should be investigated on organic substrates.
- Understand metal-polymer interactions in detail.

B. Inorganic (Metals, Ceramics, Glass) Surfaces

- Investigate the relative chemical versus mechanical contributions to adhesion to such surfaces.
- Understand the mechanism of the photochemical modification approach.
- Cross-compare acid-base characteristics derived by different methods.
- Understand interactions of silanes (adhesion promoters) with inorganic substrates using acid-base concepts.
- Explore in detail the relevance of acid-base functionalities on the surface and their adhesion to a variety of overcoats.
- Explore further the mechanism by which plasma polymerized silanes function as adhesion promoters.

10. ELECTROCHEMICAL DEPOSITION TECHNIQUES

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I. INTRODUCTION

Historically, electrochemical techniques have been used for the deposition of metals and alloys to improve the corrosion resistance or specific physical or mechanical properties. Traditional applications have been in the aerospace, automotive, oil and gas, and chemical processing industries. However, recent advances in electrochemical processing of materials and the development of novel deposition techniques have expanded the use of electrodeposition methods in these and other industries. In many cases, these advances have been related to applications in the electronics industry.

Novel materials processing has included the development of techniques for the electrodeposition of semiconductors, superconducting oxides, and conducting polymers, as well as composite films combining the properties of these materials. Electrodeposition techniques are now being used to provide specific magnetic, electrical, and electromagnetic properties; chemical and electrochemical properties, including corrosion resistance and catalytically active surfaces; and optical properties such as reflectivity and absorptivity.

This article highlights some of the novel materials and structures processed by electrochemical methods. In addition, examples of new techniques for electrodeposition are also described. Specific procedures for the electrodeposition of metals and alloys are not reviewed, but are available [1,2].

II. ELECTRODEPOSITION OF METALS

In the electronics industry, electrodeposition and autocatalytic (electroless) deposition are used in the fabrication of a wide range of components. Advances in autocatalytic deposition have resulted in the development of techniques for many applications, and commercial processes are in use for the autocatalytic deposition of nickel, copper, and gold. Electroless nickel is used in a wide range of engineering and electronics applications, and electroless copper is used in the fabrication of printed circuit boards and mirrors (as well as electroless silver). Composite coatings of electroless copper or nickel on plastic substrates have been proposed for electromagnetic interference shielding [3].

The metallization of circuit boards is carried out by additive electrodeposition techniques [4]. Typically, lithographic techniques are used in conjunction with electroless copper deposition catalyzed by a noble metal addition. Metallization has been achieved using both negative and positive resist techniques [5]. Recently, photoselective deposition of a gold catalyst has been used for the fabrication of patterned copper metallization [6], eliminating the need for a resist and reducing the number of steps required to create a patterned deposit. In related work, tin chloride has been used for the photoselective deposition of palladium as a catalyst for electroless deposition [7-9]. In integrated circuit fabrication, selective electroless deposition of Ni, Pd, and Cu has been used for contact filling, via holes, and conductor patterns [10,11].

Electroless gold is routinely used in the electronics industry for contacts, connectors, printed circuit boards, and lead frames [12] as a result of its high conductivity and corrosion resistance. Small concentrations of nickel or cobalt are commonly added to electroless gold for wear-resistant applications such as sliding contacts. Electroless gold deposits can be obtained by displacement of a less noble metal substrate, although the films are relatively thin (< 0.25 μm), because the process stops when the substrate is completely covered. More commonly, autocatalytic deposition is used for thicker and more uniform films [13].

Electroless deposition of cobalt-based alloys is used for magnetic media applications. Thin-film rigid memory disks are commercially fabricated using either electroless deposition or sputtering [14]. Typically, a magnetic cobalt-based alloy of 50-100 nm in thickness is autocatalytically deposited onto an electroless nickel-phosphorus film on an aluminum substrate. The cobalt-based alloys are generally deposited from buffered amino acid solutions with a sodium hypophosphite reducing agent producing highly uniform films with crystallite sizes on the order of 50 nm.

Another important application of electrodeposition in the electronics industry is the fabrication of ohmic contacts to semiconductor materials. For example, ohmic contacts for InP in transistor and laser applications are usually made by a vacuum process. Ohmic contacts have been formed by electroless deposition of Ni-Zn-Au on p-type InP [15] and Au-Pd on n-type InP [16]. Similarly, electroless deposits of Au-In-Pd have been used to produce ohmic contacts on GaAs.

Many industrially important metals with low equilibrium potentials, such as aluminum, titanium, and molybdenum have been electrodeposited from nonaqueous solutions. It is well known that aluminum can be electrodeposited from organic solvents (e.g., $AlBr_3$ + KBr in toluene [17,18] or $AlCl_3$ + $LiAlH_3$ in tetrahydrofurone [19]) or molten salts (e.g., $AlCl_3$/NaCl [20,21]), and commercial processes are in use. Recently, supercritical organic electrolytes have also been used to electrodeposit aluminum films [22].

New developments in techniques for electrodeposition for microelectronics applications have been related to patterned deposition or the ability to deposit selectively onto a substrate. Lithographic techniques and photoselective deposition of catalysts for electroless deposition have been described above. In other work, laser-induced deposition has been used to deposit copper and gold on both metallic and semiconductor substrates. This technique is an open-circuit process and can be used to fabricate patterned deposits without a mask [23-26]. In this case, temperature is used to modify the position of the equilibrium potential in a localized region so that electrodeposition is driven by the potential difference between this region and the nonirradiated regions. In a further modification of this technique, laser-enhanced jet plating has been used to fabricate high-density and pore-free gold deposits [27]. High-purity gold tracks have also been deposited on silicon and SiO_2 using the photoelectrochemical reduction of gaseous methyl(triethylphosphine) gold (I) [28] in which 15-60-μm-wide tracks 30-70-nm thick were deposited at a rate of 35 μm/s.

In the automobile industry, examples of recent developments include the increased use of electrodeposition of stainless steels and the fabrication of composites of electrodeposited aluminum and plastic [29]. Electrodeposition of zinc and zinc-nickel alloys is widely used for corrosion resistance, and autocatalytic deposition of nickel is used in the fabrication of a number of engine components. Novel applications for autocatalytic deposition include surface modification of plastics, e.g., conducting contacts on plastic components.

III. ELECTRODEPOSITION OF SEMICONDUCTORS

Electrochemical methods for the fabrication of semiconducting materials have received only limited attention in the literature. Most work in this area has been related to the electrodeposition of metal chalcogenides for solar energy applications. At present, there have been no techniques developed for the electrodeposition of gallium arsenide, although silicon has been deposited in small quantities from molten salts and from nonaqueous solvents with high impurity concentrations. In contrast, high-quality thin films of germanium have been prepared using relatively straightforward techniques.

A wide range of metal chalcogenide compounds has been prepared by electrodeposition. One of the first successful techniques for the deposition of compounds such as CdS and Bi_2S_3 involved anodic oxidation of the metal in an electrolyte-containing sulfide, selenite, or telluride [30,31]. Subsequently, CdSe and CdTe were deposited by reduction of the metallic ion in acidic solutions of SeO_2 and TeO_2, respectively [32-35]. However, the reduction of the chalcogenide X^{4+} to X^{2-} (where X = S, Se, Te) usually resulted in a significant fraction of the elemental form in the films. More recently [36], CdSe, CdTe, and $CdSe_xTe_{1-x}$ have been prepared from cyanide solutions containing SeO and TeO resulting in thin films with negligible concentrations of the elemental chalcogenide. High-quality polycrystalline CdS films have been prepared by the reduction of cadmium in nonaqueous sulfide solutions [37,38]. A combination of electrodeposition and reaction annealing in H_2Se has been used to prepare $CuInSe_2$ solar cells with 10%-11% efficiency [39]. More recently, photoanodes of this ternary chalcogenide have been prepared by direct electrodeposition without any subsequent heat treatment [40,41]. ZnS films have been electrodeposited from aqueous $ZnSO_4$ and Na_2S2O_3 solutions buffered to alkaline pH with NaOH [42]. Zinc reduction was suppressed by complexing with EDTA (ethylanediamene tetraacetic acid)

Of the IV-VI compounds, techniques have been developed for the electrochemical deposition of SnSe [43] and SnS [44]. Thin films of p-type SnS were electrodeposited from solutions of $SnCl_2$ and tartaric acid in ethylene glycol saturated with elemental sulfur.

In addition to the metal chalcogenides described above, a number of oxides, including Tl_2O_3, IrO_2, MoO_3, WO_3, and PbO_2, have been prepared by electrodeposition techniques. Thermodynamically, the oxide Tl_2O_3 is stable at potentials positive to the domain of stability of the soluble ion Tl^+ at certain pH values [45]. As a result, the solid oxide can be deposited by the direct electro-oxidation of the soluble ion onto a suitable substrate. Switzer et al. [46] developed a technique for photocatalytic deposition of Tl_2O_3 on silicon substrates by oxidation from alkaline Tl^+ solutions. Thin films of iridium oxide have been electrodeposited by both anodic and cathodic deposition from $IrCl_4$ in an alkaline electrolyte of hydrogen peroxide, oxalic acid and KCO_3 [47]. The deposited films were amorphous, but changed to crystalline after heat treatment at 500°C. For electrochromic applications, techniques have been developed for the electrodeposition of MoO_3 [48] and WO_3 [49] from solutions containing the dissolved metal. Doped ß-PbO_2 thin-film electrodes for electrocatalytic applications have been fabricated by electrodeposition from acidic $Pb(NO_3)_2$ solutions onto noble metal substrates [50-52].

The conditions for the electrochemical deposition of germanium were established over 40 years ago [53-55]. High-quality thin films of germanium have been prepared from $GeCl_4$ and GeI_4 in nonaqueous solvents such as glycols and polyalcohols [56,57].

Silicon deposition has been reported from both molten salts and nonaqueous solvents. Feigelson and coworkers have reported on the electrodeposition of silicon from K_2SiF_6 [58] and $BaO/SiO_2/BaF_2$ [59] melts. In the molten K_2SiF_6 electrolyte, polycrystalline films up to 3-mm thick were formed with a grain size of about 100 µm. At potentials close to the equilibrium potential, total impurity levels as low as 10 ppm were obtained. Deposition from the $BaO/SiO_2/BaF_2$ melt was analogous to the Hall process used in aluminum production. Deposition rates in excess of 100 mA/cm^2 were used to deposit 2-mm-diameter particles at a current efficiency of about 20%. These authors reported a purity of 99.97% with a room-temperature resistivity of 0.2 Ω cm, corresponding to an impurity concentration of about 10^{18} cm^{-3}.

A number of groups have reported on electrodeposition of silicon from nonaqueous solvents [60-63]. Relatively smooth, uniform films up to 200-nm thick have been deposited from $SiHCl_3$ in tetrahydrofuran [60]. However, the bulk concentration of impurities in these films was on the order of 18 at. %, much higher than that for the films deposited from the molten salts.

In the last few years, gallium arsenide solar cells have achieved relatively high energy conversion efficiencies; however, attempts to electrodeposit GaAs have been unsuccessful to date. Gallium may be electrochemically deposited from acidic or alkaline solutions when the oxide Ga_2O_3 is not stable. In the literature, there are reports of gallium deposition from acidic sulfate solutions and alkaline gallate solutions from more than 50 years ago [64-66]. In contrast, the domain of stability of elemental As is only about 0.5 V due to the formation of gaseous arsine, AsH_3, at low potentials. Despite this limited domain of stability across the pH range, As has been electrochemically deposited in acidic, neutral, and alkaline aqueous solutions under a variety of conditions [67,68]. In general, these deposits were formed at ambient temperatures and were typically 0.1-10.0-mm thick. Arsenic has been deposited under conditions of constant current from solutions of As_2O_3 dissolved in concentrated HCl [69,70]. In alkaline conditions, As has been deposited from As_2O_3 dissolved in NaOH and in KCl/Na_2CO_3 solutions [67]. Neutral solutions of As_2O_3 dissolved in KCN have also been used to electrochemically deposit As. High-quality As films over 100-mm thick have been prepared from nonaqueous solutions of $AsCl_3$ dissolved in acetone [70]. The same authors have also reported preparing even thicker films using dimethyl acetone as the solvent, although high temperatures (100°C) and high cell voltages (over 200 V at 0.1 A/cm^2) were required.

On the basis of equilibrium thermodynamic data for Ga and As [45] and taking the Gibbs free energy of formation of GaAs as -77.4 kJ/mol, a limited domain of thermodynamic stability for GaAs is predicted, corresponding closely to the domain of the stability of arsenic [71]. Although recent attempts at GaAs deposition from aqueous solutions were not successful [72], there have been no comprehensive studies using nonaqueous solvents. Polycrystalline GaSb films have been prepared by sequential deposition of Ga and Sb from aqueous solutions followed by annealing at 100°C [73].

IV. SUPERCONDUCTING OXIDES AND PEROVSKITES

Since the discovery of superconducting oxides with transition temperatures above the liquid nitrogen temperature, there has been considerable interest in the chemistry of the IIA and IIIA elements Y, Ca, Ba, and Sr. There have been a few reports of direct electrodeposition of a number of superconducting oxide precursors from nonaqueous solvents [74-76], however, in all cases, the deposited precursors required a high-temperature oxygen anneal after the deposition step. Bhattacharya et al. [74,75] reported on the electrodeposition of ~ 3-μm thick Tl-Ba-Ca-Cu-O and Y-Ba-Cu-O precursors on $SrTiO_3$ and MgO substrates using DMSO (dimethylsulfoxide) as the solvent. After annealing, these authors reported transition temperatures of 102 K for Tl-Ba-Ca-Cu-O and 76 K for Y-Ba-Cu-O films. Maxfield et al. [76] electrodeposited Bi-Sr-Ca-Cu-O and Pb-Bi-Sr-Ca-Cu-O precursors from DMSO. The post-annealed films exhibited zero resistance at 70 K and 40 K, respectively.

In an alternative approach, Zurawski et al. [77] have reported on preliminary results involving the oxidation of copper in barium hydroxide solution to form a copper oxide containing 20% barium. Konno et al. [78] have reported on the electrodeposition of $La_{1-x}Ca_xCrO_3$ precursors from chromate solutions containing $La(NO_3)_3$ and $Ca(NO_3)_2$. The precursors were converted to perovskite oxides after heat treatment above 700°C in air. Rosamilia and Miller [79] have reported on electrodeposition of sliver, copper, lead, and tin on Y-Ba-Cu-O superconducting oxides from acetonitrile. Such metallic films provide both corrosion resistance and low resistance contacts in device fabrication.

V. REFRACTORY COMPOUNDS

Recently there has been interest in the electrodeposition of refractory compounds. Electrodeposition of Mo_2C from molten salts has been reported by a number of authors [80,81]. Recent work has reported on the deposition of dense, pore-free films on nickel-plated steel substrate from an alkali molten salt of LiF/NaF/KF and K_2CO_3 with the addition of Na_2MoO_4 [80].

VI. ELECTRODEPOSITION OF CONDUCTING POLYMERS

Many aromatic heterocyclic compounds can be electrochemically oxidized at an electrode surface to form an electrically conducting polymer film. Comprehensive summaries of the fabrication and properties of conducting polymers are available [82-84]. At the present time, the main applications of research in this area are rechargeable polymer batteries, electrochromic devices, electrocatalysis, and host materials for enzymatic biosensors.

Conducting polymers can be deposited by electrochemical polymerization of the monomer under oxidizing conditions. Electrochemical polymerization has the advantage that thin-film structures can be fabricated directly onto a suitable substrate. Examples of conducting polymers that have been electrochemically synthesized include polypyrrole, polythiophene, polyacetylene, and polyaniline.

There have been a number of reports of incorporation of catalysts into thin polymer films [85,86]. These modified electrodes have been shown to exhibit higher efficiencies and durability than adsorbed monolayers. The polymer film provides a host material of high conductivity, and the catalyst is incorporated at the electrode surface in relatively high concentrations.

VII. COMPOSITE MATERIALS

A. Multilayer Structures

Thin-film multilayer structures represent a new class of materials,. many of which exhibit unique optical, electrical, magnetic, and mechanical properties. Electrodeposition has been used to fabricate compositionally modulated metallic multilayer structures of Cu-Ni, Cu-Co, Cu-Pd, Ag-Cu, Ag-Pd, and Au-Ni [87-89]. These materials are of interest for their mechanical and magnetic properties. Recently, Switzer et al. [90] have reported preliminary results on the electrodeposition of compositionally modulated $Tl_aPb_bO_c$ structures with modulation wavelengths on the order of 5 nm.

A schematic diagram of this type of structure is shown in Fig. 1a. The two components, A and B, are deposited sequentially, either by sputtering or electrodeposition, to form a multilayer structure with a characteristic wavelength, λ.

B. One-Dimensional Structures

Composite structures consisting of a metal wire within an inert host material have been used for applications such as magnetic recording media [91-94] and grid-type micropolarizers [95]. These structures are shown schematically in Fig. 1b. An effective method for producing such structures is by electrodeposition of the metal or alloy into a porous material. Several groups have reported fabricating magnetic recording media by electrodeposition of iron [91-93] and cobalt alloys [94] into 3-4-μm-thick porous anodized aluminum oxide.

Encapsulated wire electrodes are routinely used as microelectrodes for applications in electroanalytical chemistry. In many cases, single disk electrodes are fabricated by electrodeposition of a metal such as gold or platinum into a glass capillary of 1-10-μm diameter [96]. In related work, Penner and Martin [97] have reported on the electrodeposition of platinum into 200-nm-diameter pores in polycarbonate membranes (Nuclepore, Inc.). Similar techniques have been used to fabricate wires of conducting polymers, as described in the next section.

C. Composite Polymer Films

Several researchers have reported on electropolymerization of conducting polymers into microporous materials. Penner and Martin [98] electrodeposited polypyrrole into 1-μm-diameter cylindrical pores in polycarbonate membranes. The conductivity of these highly oriented polymer fibers was reported to be as much as an order of magnitude larger than that of a thin film of the same thickness.

There have been a number of reports of electropolymerization of polyaniline in insulating polymeric host materials [99,100]. Similar results have been achieved by chemical polymerization of a conducting polymer in a host material [101]. Orata and Buttry [99] electropolymerized polyaniline in a solution-cast Nafion (E. I. DuPont de Nemours and Co.) film. These composite films were fabricated by solution-casting Nafion and aniline in an appropriate solvent followed by electropolymerization of the aniline to form an interconnected network of the conducting polymer through the host matrix. These composite films are reported to have higher conductivities and faster switching rates due to enhanced proton transport. This type of composite structure is shown schematically in Fig. 1c.

Bard and coworkers [102] have reported on the deposition of silver and copper in a thin film of an ionic conductor using a scanning tunneling microscope (STM). The STM tip was used as a counter electrode with a metallic substrate serving as a working electrode. A Nafion film was used as the electrolyte and soaked in solution of silver or copper ions prior to deposition. The metal ions in the film were reduced under conditions of constant potential, and tracks about 0.1-μm wide could be written into the Nafion film by using the translational stage of the STM.

D. Particulate Composites

The fabrication of particulate composite materials can be achieved through electrodeposition of the metallic host in an electrolyte containing the second phase particulate material. This technique has been developed commercially in the last few years for the fabrication of wear-resistant coatings by incorporation of relatively large-diameter particles (on the order of 1-10 μm). These structures are shown schematically in Fig. 1d.

For the electrodeposition of particulate composites, the only requirement is that the second phase can form a stable suspension in the electrolyte. Examples of the particulates include carbides [103-105], oxides [104,106], and diamond [107]. For electrodeposited composites of relatively large particle size (> 1 μm), volume fractions of the particulate in the range of 0%-30% have been reported.

Autocatalytic deposition of nickel has also been used to fabricate composite Ni/polytetrafluoroethylene (PTFE) films using ~ 1-μm PTFE particles [108,109]. Indeed, Ni/PTFE composites are used commercially in a number of aerospace, electronics, and automotive applications due to their enhanced wear resistance and relatively low cost. Composite Ni/Cr_3C_2 films have been fabricated by autocatalytic deposition of nickel from an electrolyte containing Cr_3C_2 particles 2-3 μm in diameter [110].

In addition to research into composites with relatively large particles (> 1 μm), there has been some work directed toward composites with submicron particles. For example, Au/Al_2O_3 composites have been electrodeposited using 50-nm alumina particles [111].

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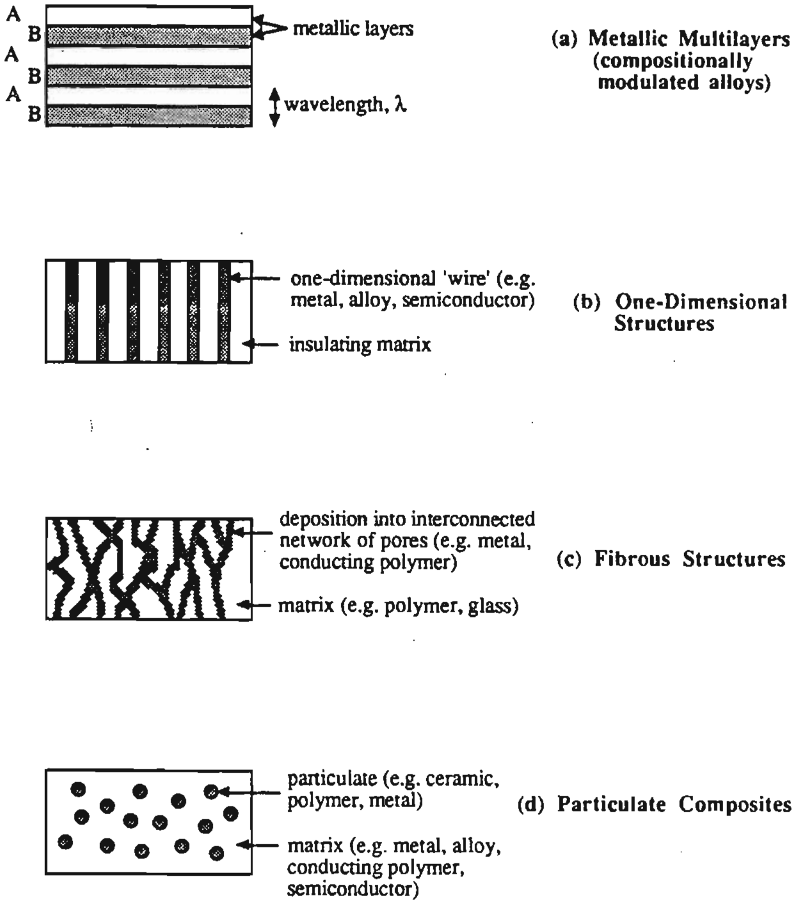

Figure 1. Electrochemically processed composite structures

11. PLASMA-AIDED MANUFACTURING

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ABSTRACT

Plasma-aided manufacturing, the use of electrically charged particles in the manufacturing process, is used for producing new materials with unusual and superior properties, developing new chemical compounds and processes, machining, and altering and refining materials and surfaces. It has direct applications to semiconductor fabrication, materials synthesis, welding, lighting, polymers, anti-corrosion coatings, machine tools, metallurgy, electrical and electronics devices, hazardous waste removal, high-performance ceramics, and many other items in both high-technology and the more "traditional" industries. This paper describes the nature of plasma-aided manufacturing and how it applies to materials coating.

I. INTRODUCTION

Plasma-aided manufacturing, which we define as the use of electrically charged particles in the manufacturing process, is an emerging field that will greatly enhance the international competitiveness of American industry. Plasma-aided manufacturing is used for producing new materials with unusual and superior properties, for developing new chemical compounds and processes, for machining, and for altering and refining materials and surfaces.

In order for plasma technology to be utilized in manufacturing, it is necessary that the processing result be unattainable by other methods, superior products results, or the plasma technology be more economical. Plasma-aided manufacturing is now at a critical point in its development. In the past, it has been possible to produce "industrial" plasmas for use in plasma-aided manufacturing with limited knowledge of the plasmas, their chemistry, their specific process control, quality and productivity improvement, and sophisticated production techniques. Now our industrial colleagues tell us that, without an in-depth understanding of the variety of phenomena taking place and their application to the industrial environment, advances in this technology, and its efficient use, will occur at a diminishing rate. Specifically, our partners have expressed concerns about yields, end-point detection, reliability, processing rate, aging, and the feasibility of using various plasma processes. Our partners believe that significant progress demands a cross-disciplinary effort beyond the capability of any single existing U.S. industrial or university research group.

An illustrative diagram of the various reactions taking place in a plasma processing reactor is shown in Fig. 1.

Every plasma reactor incorporates the following processes:

- Electron impact ionization and dissociation
- Gas phase chemical reactions
- Surface phase chemical reactions.

To maintain the discharge, ionization must occur to sustain the plasma. Electrons are needed to dissociate the feedstock gases to produce fragmented neutrals that are chemically active (free radicals). In addition, the ions are often needed, either by themselves or in conjunction with other species in the plasma, to produce the needed chemical reactions, either in the plasma itself or on the surface of the material to be processed. Often, the gas-phase chemical reactions tend to be a loss mechanism for the free radicals produced, serving much as do the recombination processes for charged particles. On the surface itself, very complex processes occur that are often difficult to quantify; in these processes, the free radicals, ions, and other particles impinge on the surface causing implantation, sputtering, or etching, or a combination of a number of these processes.

When plasmas are utilized in manufacturing, the application and character of the processes involved are governed by the operating pressure of the system. Typical reactors cover operating pressures from below 10^{-4} Torr to greater than atmospheric pressure. Figure 2 shows the types of processes used in manufacturing as a function of the operating pressure of the reactor. At low pressures, physical rather than chemical effects dominate. This is the case in plasma source ion implantation, for example. As the pressure increases, sputtering occurs, and then chemical effects, such as etching, begin to become significant. At higher pressures, deposition effects tend to dominate, and at the highest pressures, as in thermal plasma spraying, chemical vapor deposition (CVD), and arc-spray coating, the plasma tends to be utilized primarily as a heat (thermal) source. Viewed in this way, it can be seen that there are many connections that occur between the various processes. Each of them, for example, has surface and materials issues. Each process needs to know the gas and surface temperatures and the densities of the various species making up the plasma. Each needs to develop a modeling capability that can predict the properties of the materials being processed.

Accordingly, the relationship between the "external" process variables, such as radio frequency (RF) power, gas pressure, gas flow rate, etc., which are variables that can be set externally to the reactor, and the "internal" process variables, such as charged particles, free radical and neutral particle concentrations, and fluxes, need to be determined. An example of how plasma deposition might be treated in this way is shown in Fig. 3.

II. COATING TECHNOLOGIES

For plasma-aided manufacturing to have an impact on present and future requirements of industry, new processes, diagnostics, sensors, modeling, and statistical and control strategies need to be developed. In addition, new studies in basic science and engineering are also needed.

Advances in the research base will contribute new insight for the long-term improvement of plasma-aided manufacturing. In connection with monitoring and control of the manufacturing processes, for example, four important plasma diagnostics have not routinely been used in industry for control and monitoring. They are: laser-induced fluorescence [1], infrared diode laser absorption [2], vacuum ultraviolet (VUV) emission as well as Fourier transform infrared spectroscopy, and in situ ellipsometry.

Advances must also be made toward a better understanding of nucleation, growth, surface diffusion, interfacial roughness, stress, and surface chemistry of plasma-deposited films. The influence of plasma processing parameters on these properties may be determined by using a variety of these in situ diagnostics. Particular attention will be directed toward understanding the plasma chemistry. Efforts will be directed toward modeling of film growth in the plasma environment based on statistical design techniques. Specifically, the influence of (1) film thickness, density, and stress on optical properties, (2) plasma modification of surfaces, and (3) growth of external polymeric surfaces needs to be determined.

Problems in the current technology associated with plasma-aided manufacturing are: the lack of process reliability and optimization, the lack of an engineering base with which to develop process control and transfer the technology to industry, and a limited knowledge to further expand the applications of the processes.

The research goal for plasma-aided manufacturing is to develop the diagnostics, modeling, and control techniques necessary to utilize these processes effectively in industry. We believe that the techniques will have applications to a wide variety of plasma deposition processes in one laboratory. It is necessary to emphasize only a nominal number of processes because there are a very large number of potential applications. Following is a brief discussion of a number of plasma coating processes and current research efforts in the Engineering Research Center (ERC) for Plasma-Aided Manufacturing.

A. Plasma Polymerization

In the ERC, a parallel-plate 13 MHz reactor called P4 (parallel-plate plasma polymerization) is an engineering test bed for plasma polymerization. P4 is shown in Fig. 4. It has been designed to ensure compatibility with the various diagnostic tools being developed in the ERC. It is also computer-controlled to facilitate the real-time control of the deposition process and the acquisition of diagnostic data. The current material under test in this system is polymethylmethacrylate (PMMA). This material is deposited on silicon substrates that can either be coated with a conducting or insulating film or can be uncoated. The deposition pressure is approximately 100 mTorr. Subsequent modifications to the reactor will include the use of electron cyclotron resonance (ECR), RF induction, and/or magnetically-confined plasma sources.

P4 is outfitted with a personal computer (PC)-based controller so that automated deposition processes are possible. This facilitates statistical experiments and the use of statistical process control. Diagnostics include Langmuir probes, optical emission spectroscopy, laser-induced fluorescence, and mass spectrometry, and they allow the determination of electron temperatures and densities, reactive species present, and their concentrations and plasma potential. These data will be used in conjunction with plasma modeling to help understand the plasma kinetics and the surface and growth kinetics of the plasma polymer. The modeling effort uses a particle-in-cell approach to model plasma kinetics. Statistical techniques will be used to determine how the plasma process parameters (such as power, flow rate, and pressure) are related to the internal plasma parameters (such as electron density and temperature) and how the plasma process parameters are related to the desired materials properties (such as refractive index, dielectric behavior, and residual stress). Given this information, it will be possible to tailor the material properties of the deposited polymer films [3]. In particular, we plan to fabricate polymer channel waveguides with graded indices of refraction for waveshaping applications in photonics. To achieve this goal, we need to deposit films on the order of 5-10-µm thick. This will require that the deposited films have minimal residual stress. A major research goal is to utilize statistics, diagnostics, and modeling tools to develop a mechanistic model for residual stress in PPMMA films.

B. ECR Deposition

This activity is a collaborative effort between the ERC and several industrial partners. We are optimizing the deposition using ECR plasmas to ensure the desired materials properties of the deposited films. The materials systems of interest are alternate vapor sources for the deposition of silicon compounds. The source most frequently used now, silane, presents safety hazards because it is exposed to ambient air. ECR has a number of promising advantages for deposition, and we expect to determine and optimize its effectiveness by using the diagnostics and modeling methods made available through the ERC.

One industrial partner will provide the ERC with a number of novel liquid vapor sources to use as silane gas substitutes in the ECR deposition of silicon nitride; this is of great interest to semiconductor manufacturers. The ERC diagnostics will be used to develop an understanding of the nitride deposition process. In particular, as the chemical kinetics are understood, we expect to interact with our industrial colleagues to design more advanced molecules that will minimize unwanted free-radical composition. The deposited films will be characterized using facilities available on campus. The chemical composition will be investigated using Auger electron spectroscopy and electron spectroscopy for chemical analysis (ESCA). The refractive index in the visible will be measured with a three-color ellipsometer, and the dielectric behavior will be characterized using a capacitance-voltage system.

C. Plasma-Deposited Barrier Coatings

Several industrial partners have expressed an interest in developing plasma-deposited sources and processes for surface-selective deposition of barrier coatings in or on forms of varying shape and scale. Barrier coatings are required on certain containers to prevent the permeation of gases such as oxygen through container walls or to prevent the escape of vapors out of the container. In certain cases, plasma-deposited coatings have either a processing or a performance advantage over conventional methods such as co-extrusion and wet or gas chemical deposition. As an example, plasma-deposited polymer coatings are highly cross-linked, and the deposition process does not produce substantial amounts of chemical waste, as does a wet chemistry process. Unfortunately, however, many plasma source systems do not physically deposit coatings that conform to the odd shapes of tubes, bottles, and other hollow and re-entrant forms.

We are investigating plasma deposition of barrier coatings with several RF capacitive and inductive plasma sources. Working with our industrial partners, we will apply our expertise in plasma engineering to design sources and processes directed toward a number of contemporary manufacturing goals. Our activities will draw from nearly every facility and support group within the ERC. Plasma source design and construction will require RF electromagnetic field modeling, two-dimensional (2-D) plasma modeling, and much of the Center's plasma diagnostic capabilities, such as electric probes, optical-emission spectroscopy, infrarede (IR) spectroscopy, and mass spectrometry. Process development will require film characterization studies, statistical experimental design, and testing of surface-barrier aging and performance. By placing the source design directly within the context of our partners' industrial applications, we will ensure the transfer of technology and engineering advances.

D. Plasma Modification of Fibrous Material

The goal of this work is to modify the surface characteristics of textiles and composites, while leaving their bulk properties and appearance unaffected. By controlling the composition of the plasma, the surface of the polymer can be tailored for a specific end use. Previous work has been done to improve the interfacial bonding properties of carbon, Kevlar®, glass, polyethylene, polyester, and other thermoplastic fibers.

The primary direction to be followed here is to improve the surface characteristics of fibrous materials (textile materials and composites) for wettability (both hydrophilicity and hydrophobicity), static and soil resistance, printing, and dyeability. Compared to other treatments, plasma processing offers the following potential advantages: lower cost, lower total energy consumption, less required space, more rapid treatment, a decrease in process liquids, higher reproducibility, and less toxicity.

The research will compare the properties of plasma, chemically treated, and untreated materials. Their surface and chemical and aging properties will be measured and compared using the diagnostics available in the ERC. Engineering statistics will be used to optimize the plasma process. The common plasma diagnostics and modeling developed for all of the projects in the deposition and polymerization area will be employed to determine the plasma properties required for effective treatment. Subsequently, we will examine the feasibility of scaling up the process to a manufacturing environment.

E. Plasma Spraying

A three-pronged approach will be followed by advancing the knowledge base through diagnostics and modeling of the plasma-particle interaction and of the dependence of plasma jet fluid dynamics on the spray nozzle design, enhancing the technology base by obtaining empirical correlations between coating characteristics and spray process parameters using statistical experimental design methodology, and making use of any advances in our understanding through the testing of equipment and/or process improvements. Figure 5 shows a diagram of the ERC-developed Hot Anode Gas Shielded (HAGS) [4] plasma torch, which has a higher power efficiency than a conventional DC torch of a similar design. Full implementation of the HAGS torch will result in more efficient use of electrical power, improved coating quality, and more rapid coating deposition rates.

F. Thermal Plasma CVD

Thermal Plasma CVD is particularly useful for materials that do not have a liquid phase. Our focus in this new technology is on obtaining a detailed understanding of selected processes that have both immediate industrial interest and specific diagnostic value. We are particularly interested in high-rate deposition of diamond film, high T_c superconducting films [5], and nonoxide ceramic films such as SiC and BN. Three parallel efforts are being pursued: a combination of diagnostics and modeling to clarify the mass transport across the nonequilibrium boundary layer between plasma and substrate and the nucleation on the substrate surface, a statistical experimental design approach for obtaining correlations between coating characteristics and operating parameters, and a materials characterization study of the interface between coating and substrate that will link the defects in the film with deposition parameters.

G. Plasma Modification of Materials

The goal of this activity is the development of new, cost-effective ion implantation techniques fo improving the surface properties of materials, called plasma source ion implantation [6] (PSII), a patented non-line-of-sight technique for ion implantation of surfaces to improve the wear, corrosion, hardness, an fatigue properties of materials. A diagram of a PSII reactor is shown in Fig. 6.

Two areas for developing methods for the plasma modification of materials are important: (1) surface hardening and wear resistance and (2) corrosion and oxidation resistance. Preliminary testing has demonstrated that implantation of nitrogen ions by PSII can substantially improve the surface hardness and wear resistance of certain materials in certain environments, but the applications are quite limited. Nitrogen ion implantation is generally effective in increasing the surface hardness and wear resistance for steels with high chromium content in wear applications at low to moderate temperatures. Thus, although some of the material problems of industrial interest are amenable to nitrogen implantation with the present PSII facility, the facility is unable to produce implantation processes that address applications such as (1) the surface hardness and wear resistance of low chromium steels, (2) the surface hardness and wear resistance of ceramics and other nonsteels, (3) the hardness and wear in high-temperature environments, (4) corrosion resistance, and (5) oxidation resistance. For these broader applications, ion species such as titanium, carbon, chromium, etc., will be required. To address these problems, we are extending the PSII process to operate in a molecular ion species mode and modes similar to the IBED (Ion Beam Enhanced Deposition) or ion beam mixing techniques that have been developed using conventional technology. In these latter techniques, a thin layer of a desired nongaseous implant species such as titanium is deposited onto the target (for example, from sputtering or by physical vapor deposition), and then bombarded with energetic ions (for example, nitrogen or noble gas ions).

We treat three classes of targets: laboratory test coupon specimens, manufactured components, and manufacturing tools. The test coupons are characterized by Auger electron spectroscopy (AES), transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning Auger microscopy (SAM), Rutherford backscattering spectroscopy (RBS), and X-ray photoelectron spectroscopy (XPS) or ESCA, as well as optical microscopy, microhardness, and pin-on-disk tribology tests for relative wear resistance. The manufactured components and manufacturing tools that are sent out for field testing are often either too large or otherwise unsuitable for detailed surface characterization, but as a minimum we try to characterize at least the microhardness of the components before and after implantation.

Both the laboratory tests and the industrial field tests are necessary. The work on laboratory test coupons represents the development of the knowledge base of the PSII process, whereas the field test work contributes to the technology base. The test coupon experiments are crucially important in our long-range strategic development plans for developing new industrial processes. The field test experiments are important because they validate the test coupon experiments and ensure that the test coupon experiments are leading to valid industrial processes.

An important aspect of the development activity is the modeling activity that supports the experimental work. The modeling is done in three areas: plasma physics studies of the PSII sheath scaling, Monte-Carlo calculations of the resulting ion-materials interactions, and tribological modeling of ion-implanted specimens.

Plasma modification of materials depends crucially on the interaction of a broad spectrum of disciplines including plasma physics, mechanical and microstructural properties of materials, tribology, corrosion chemistry, radiation interaction with matter, and manufacturing systems analysis. These disciplines are tightly interwoven; the results of plasma physics modeling codes are used as input to the ion-materials interaction modeling codes that we use to predict implanted ion profiles. The implanted specimens are then characterized by a variety of surface analytical and tribological techniques. Finally, tribological modeling is used to close the loop.

A major obstacle that currently hampers the progress of plasma modeling of the PSII process is the lack of diagnostics to measure the composition of the ion species in the PSII plasmas. The species composition must be known to provide input data to the modeling codes for the ion-materials interaction studies. Rough estimates of the species composition can be obtained from other experiments and from indirect measurements of the Auger profile distributions of implanted ions. For example, in nitrogen plasmas, modeling gives the best agreement with the Auger profiles for a species mix of approximately 65% N_2^+ and 35% N^+, but the error bars are very large, and a better understanding will be required for the IBED development. Another diagnostic need is a noninvasive technique to complement the probe measurements of sheath propagation. To address these needs, the ion species composition of the PSII plasma species must be measured, and we have chosen the laser-induced fluorescence (LIF) diagnostic on the new PSII system as an initial step in this direction.

Besides continuing analytic modeling, we also continue the development of detailed plasma simulation codes. One code being developed uses the propagator (or Green's function) solution of the plasma kinetic equation. The program includes all the relevant atomic physics as well as electron emission at the target and the chamber wall. The first implementation of the program will probably be for a helium plasma, followed by versions for nitrogen and other plasmas.

Another code is now capable of predicting the energy spectrum of bombarding ions. We will compare these predictions with experimental measurements of two types: indirectly, by ex situ Auger profiling of silicon wafer test coupons, and directly, using a telemetered energy analyzer inside a model target. Two-dimensional (2-D) as well as three-dimensional (3-D) codes are needed to model the PSII treatment of targets. As these codes evolve, they will be compared with 2-D and 3-D measurements that are just now beginning to yield results.

H. Semiconductor Applications of PSII

Although PSII was originally conceived as an ion implantation process for nonsemiconductor applications, it has been demonstrated that there are many very good applications of PSII in semiconductor processing. PSII achieves in a bell jar type of environment the same ion implantation treatment previously available only with beamline accelerator technology. This opens up the possibility of incorporating the ion implantation process into other processes, e.g., to do in a single chamber both ion implantation and plasma etching. PSII has particular advantages in the intermediate energy range from 1 keV to 20 keV; these energies are not well suited to either plasma etching processes at the low end or to beamline implanters at the high end. Specific examples of PSII applications that might be attractive include backside impurity gettering, shallow implants, ion implantation with rapid thermal annealing, and formation of insulating layers of AlN.

ACKNOWLEDGMENTS

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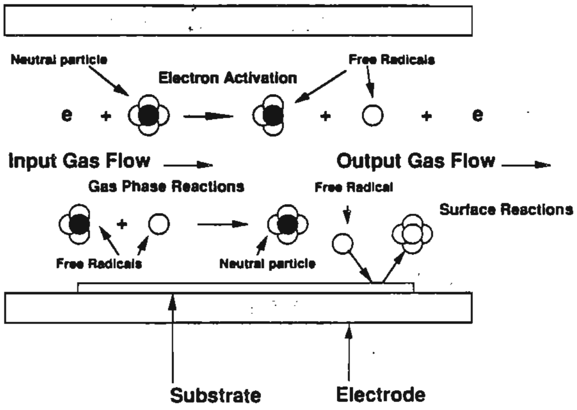


Figure 1. Processes occurring in a plasma reactor

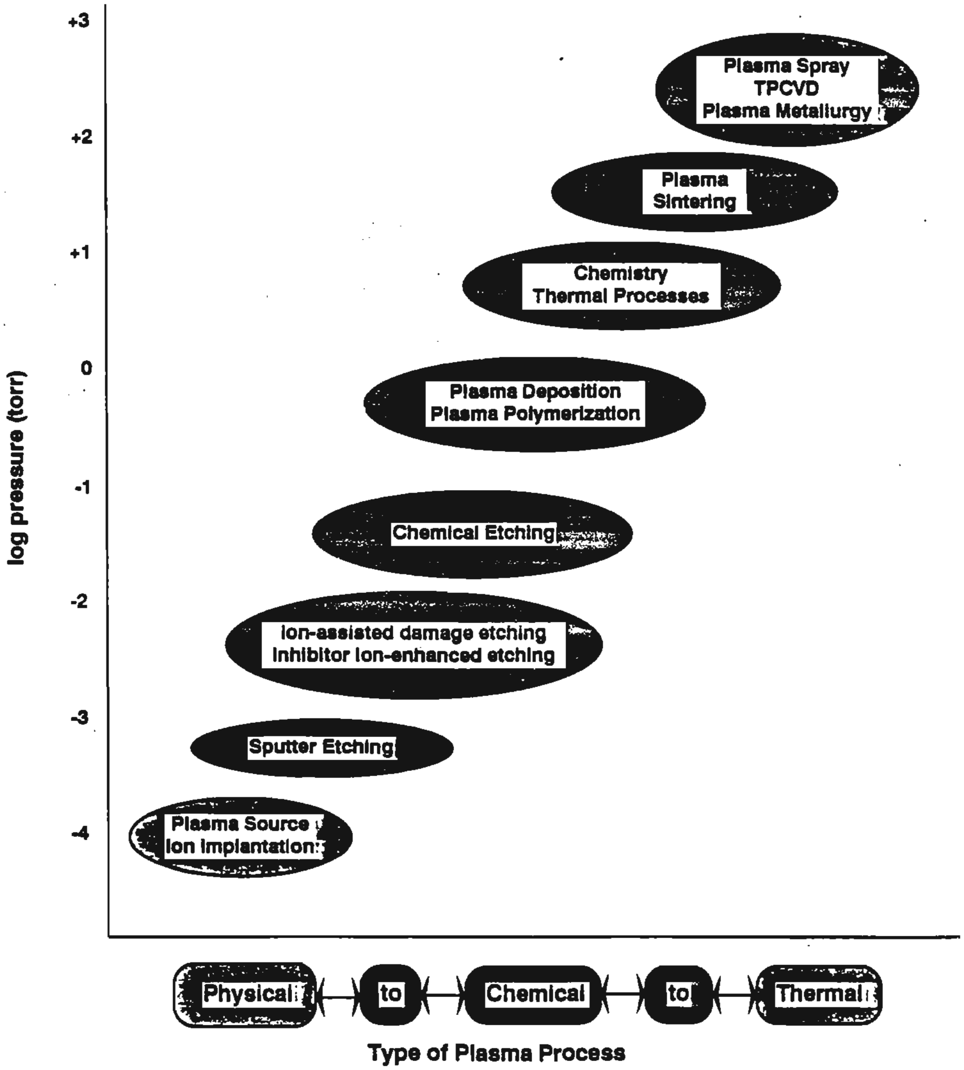
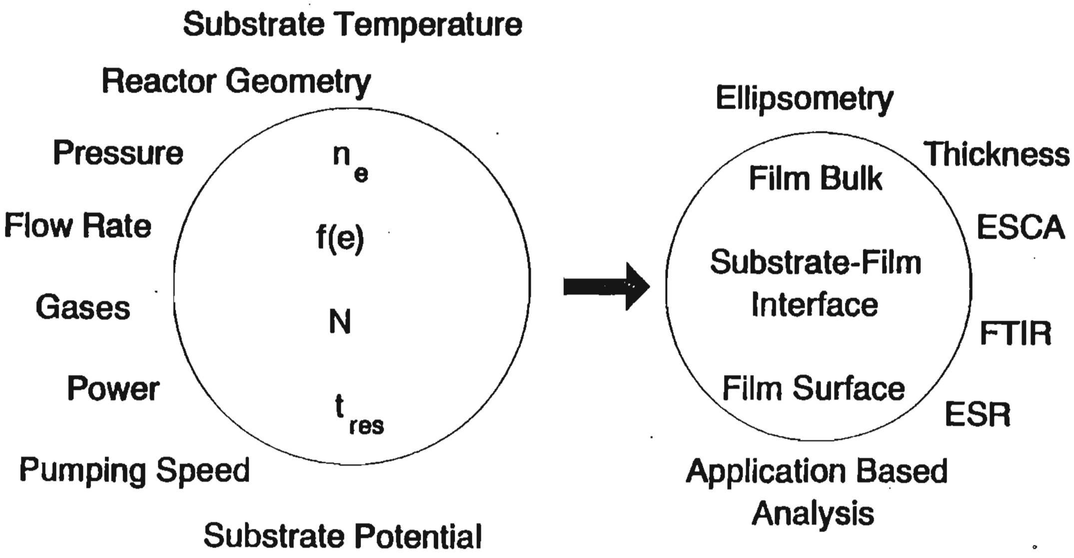


Figure 2. Types of plasma processes. As the pressure increases, the nature of the processes tends to change from physical to chemical to thermal, but in general, each process occurs in a varying degree.

Internal vs. External Parameters



Substrate Temperature

Reactor Geometry

Pressure

Flow Rate

Gases

Power

Pumping Speed

Substrate Potential

n_e

f(e)

N

t_{res}

Ellipsometry

Film Bulk

Substrate-Film Interface

Film Surface

Thickness

ESCA

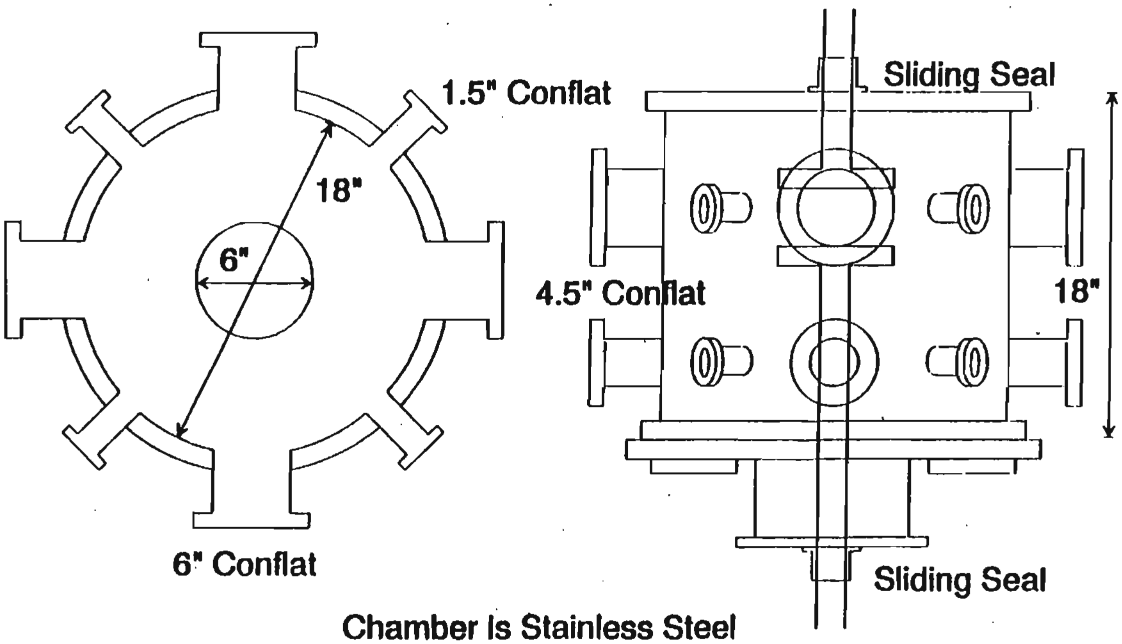
FTIR

ESR

Application Based Analysis

Figure 3. Relation between internal and external process variables

Chamber Design



Chamber Is Stainless Steel

Figure 4. The P4 polymerization reactor

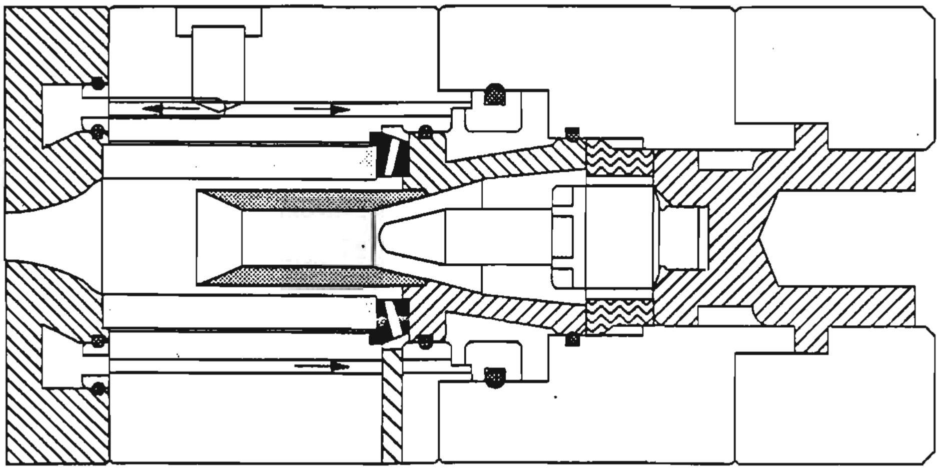


Figure 5. The HAGS plasma torch

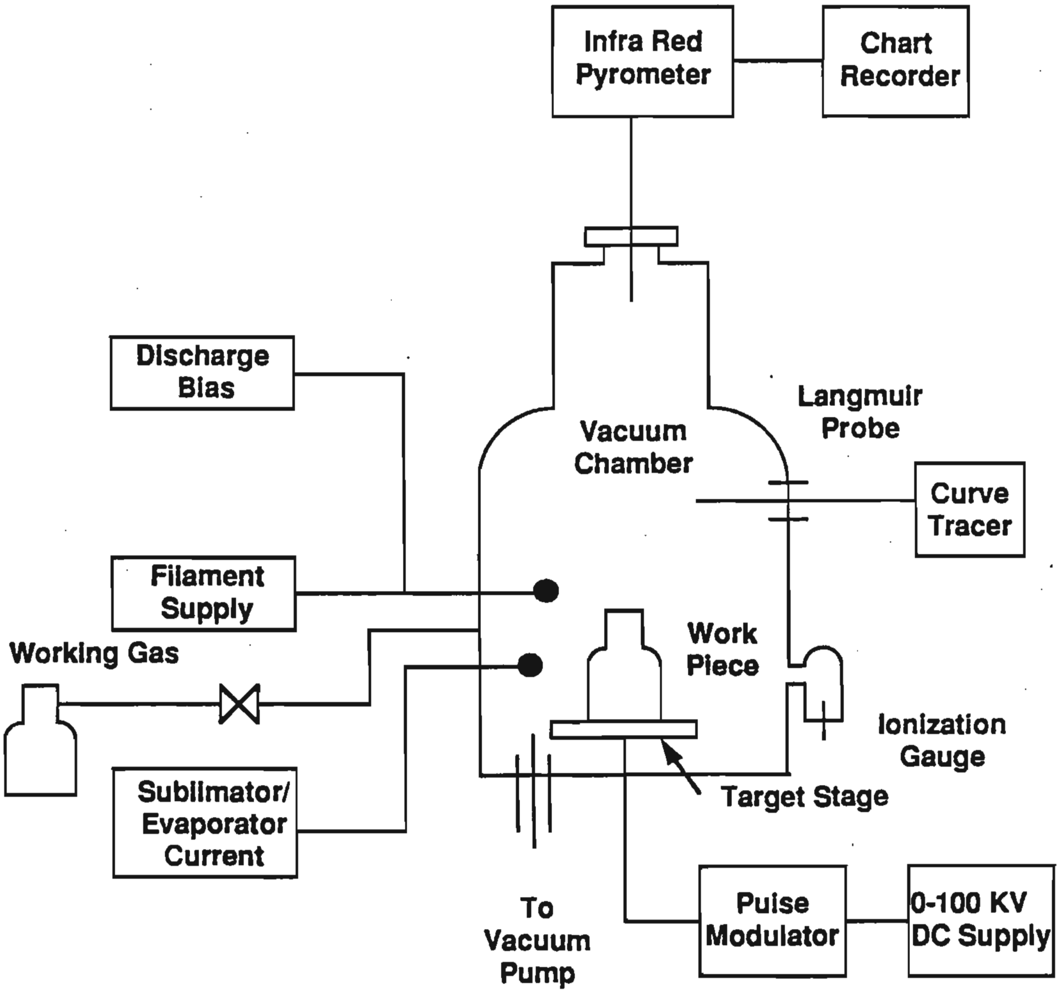


Figure 6. PSII system

12. ATOMISTIC INORGANIC FILM FORMATION BY REACTIVE AND NONREACTIVE PVD TECHNIQUES

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I. INTRODUCTION

Physical Vapor Deposition (PVD) is defined as an atomistic deposition process in which atoms (sometimes molecules) are transported from a solid or liquid surface (source) to condense on another surface (substrate) without gas phase nucleation or reaction. Generally the source for depositing atoms is thermal vaporization or physical sputtering. Figure 1 depicts the various forms of PVD processing techniques.

II. PVD TECHNIQUES

A. Vacuum Deposition

Vacuum deposition (evaporation) is typically defined as a deposition process in which the atoms (or particles) from a thermal vaporization source reach the substrate without collisions with residual gas molecules. This normally requires a vacuum of better than about 10^{-4} Torr (1.3×10^{-2} Pa). This definition does not address the effects of generally undesirable concurrent bombardment of the substrate by residual reactive gases, the avoidance of which often requires high (10^{-7} Torr) or ultrahigh (10^{-9} Torr) vacuum depending on the deposition rate, the reactivity of the species, and the impurity level of the desired deposit. Ultrahigh vacuum (UHV) conditions are used in the molecular beam epitaxy (MBE) deposition of semiconductor materials whereas high or even a poor vacuum condition can be used for evaporation processing in which contamination is not a major problem either because of the materials involved, the high rate of deposition, or the materials requirements.

The adatoms that impinge on the substrate surface have a line-of-sight direction from the source and thermal energies. When alloys are vaporized, the materials vaporize in proportion to their vapor pressures, which may differ greatly with materials and which are strongly dependent on the source temperature. When compounds are vaporized, there is often a loss of one constituent on condensation.

The advantages of vacuum deposition are that the

- Techniques and equipment are relatively simple
- Source material may be relatively inexpensive
- Contamination level may be made very low
- Environment may be easily monitored
- Deposition rates may be easily monitored
- Deposition rate is high

- Shutters may be used to advantage in the system.

The disadvantages of vacuum deposition are that the

- Line-of-sight deposition gives geometrical shadowing of surface features
- Point source for deposition can make deposition uniformity a problem
- Films are often not fully dense and may have high residual tensile stresses
- Compounds and alloys are difficult to deposit with a controlled composition
- Deposition rate may be highly variable during a "run" or from run to run
- In situ substrate cleaning is not common but can be done by plasma techniques
- Technique is often used with poorly trained personnel and marginal equipment.

B. Sputter Deposition

Sputter deposition, which is often called sputtering and is a poorly chosen term, is the deposition of particles whose origin is a surface ("target") being sputtered, usually by accelerated ions. One of the major advantages of sputter deposition is that the deposition rate is rather constant and reproducible and can be sustained over a long period of time. The sputtering process allows alloys to be easily deposited from an alloy source and compounds to be deposited using a reactive plasma deposition environment or a reactive plasma or ion beam to give concurrent bombardment of the target material. There are a number of different sputtering techniques and configurations amenable to sputter deposition. A problem with many of the sputter deposition configurations is obtaining a uniform deposit over large areas, which requires a uniform plasma that is difficult to attain in many sputtering configurations, particularly magnetron sputtering.

Sputtering may be done in a "high pressure" plasma in which the sputtered particles are thermalized by gas phase collisions before they reach the substrate, in a "low pressure" plasma in which thermalization does not occur because the sputtered particles reach the substrate with their sputter-ejection energies that are much higher than thermal or in a vacuum (using ion guns for sputtering) in which gas-phase collisions do not occur. In the case of "low pressure" and vacuum deposition environments, high-energy reflected neutrals from the target may concurrently bombard the depositing film. This high-energy reflected neutral bombardment is often poorly controlled.

If a reactive gas (deliberate or contaminant) is present in the plasma, it is chemically "activated" (radicals and ions) by fragmentation to be more reactive with the depositing material. This allows "reactive deposition" of compounds. The most desirable case is one in which of the constituents is condensible and the other is gaseous ($Ti + N \Longrightarrow TiN$). In many cases of reactive deposition, it has been difficult to obtain fully reacted material so that the compounds are substoichiometric (e.g., TiN_{1-x}). In reactive sputter deposition, plasma uniformity and reactive species availability are very important for obtaining a uniform film.

Sputter-deposited films are often not fully dense. Film density may be increased and the stoichiometry controlled by concurrent bombardment during deposition. See Section C.

The advantages of sputter deposition are having a

- Long-term, stable vaporization source
- Large-area source with some configurations (direct current [DC] diode)
- Unique source with some configurations (parallel line sources for planar magnetron and rotatable tubular sources)
- Source of materials that may be easily deposited as alloys
- Reactive deposition capability that allows the deposition of compounds
- Scheme for easy in situ substrate cleaning and surface preparation.

The disadvantages of sputter deposition are that

- Films are often not fully dense
- Reactively deposited films may not be fully reacted (substoichiometric)
- Sputter-deposited films may have a high residual tensile or compressive stress
- Many process variables need to be controlled
- Most of process energy goes into heating the target
- Plasma contamination is often a process variable that is difficult to control
- Sputtering sources are expensive
- Deposition rates are generally slower than for vacuum evaporation.

C. Ion Plating

Ion plating is a generic term for deposition processes in which concurrent energetic particle bombardment during deposition is used to modify the composition, morphology, microstructure, and properties of the deposited material. The source of depositing species may come from thermal vaporization, sputtering, or chemical vapor precursor species.

There are two basic versions of the ion plating process. In plasma-based ion plating, the substrate is in contact with a plasma, and the ions are accelerated from the plasma and arrive at the surface with a spectrum of energies. In addition, the surface is exposed to an activated species from the plasma, adsorption of gaseous species, high electron concentrations, and radiation from the plasma. In the vacuum-based ion plating often called "Ion Assisted Deposition" (IAD), "Ion Beam Assisted Deposition" (IBAD) or "Ion Beam Enhanced Deposition" (IBED), the bombardment is from a beam of ions formed in an ion gun and accelerated to the surface with a more specific and controlled energy distribution often accompanied by an undefined bombardment by high-energy reflected neutrals when a sputtering source is used. Many of the surface effects of the two versions are the same, but there are also important differences to be expected, particularly in reactive deposition and surface coverage.

The most common sources for energetic bombarding particles at gas (plasma) pressures above which there is thermalization of energetic particles between the vaporization source and the substrate are

- Ions from a DC, radio frequency (RF), plasma arc, or laser-induced plasma being accelerated to the surface under an applied bias or "self-bias"
- High-energy neutrals originating from charge exchange processes in a gas.

When the pressure is low enough to assure little or no thermalization between the source and the substrate, additional sources of energetic particles are

- Reflected high-energy neutrals that arise from energetic ions reflecting from a surface as neutrals, e.g., low-pressure magnetron sputtering and ion beam sputtering
- Acceleration of ions from the vacuum arc vapor source due to a space charge
- Acceleration of negative ions (e.g., O^-) away from a negatively biased sputtering surface
- Energetic neutral sputtered species
- Ion guns in which ions are extracted from a confined plasma using a grid system.

The flux and energy of the bombarding species are very important. High-energy particles are incorporated into the lattice and may precipitate to form voids (lower density). The high-energy particles also tend to give high residual compressive stresses in the films by excessive "recoil implantation" of surface atoms. In order to obtain dense, low-stress films, the bombardment energies should be around 100-250 eV with a flux ratio (energetic particles to depositing atoms) of about 1:10.

Important ion plating deposition parameters are: energetic particle to depositing particle ratio, energy of the bombarding particles, ambient gas/plasma pressure and composition, deposition temperature, and the materials involved. In reactive ion plating, in which a compound film material is formed, the bombardment and deposition parameters affect the reaction kinetics and degree of reaction, phase and stoichiometry of the compound, crystallographic orientation, and inclusion of unreacted species. Additional factors affecting the surface reactions include: chemical state of depositing, ambient and bombarding particles, surface heating, defect production, surface adsorption, implantation, nucleation density of depositing species, secondary electron emission, and preferential sputtering and desorption of surface material.

The advantages of ion plating include obtaining

- Control of film properties such as density and stress by controlled bombardment
- Bombardment-enhanced chemical reactions and removal of unreacted species
- Good surface coverage
- Good adhesion and interface formation
- High deposition rates using thermal vaporization sources.

The disadvantages of the ion plating process include the

- Many process parameters
- Inclusion of bombarding species in the film if uncontrolled
- High compressive film stresses if uncontrolled
- Poor understanding of surface processes in ion plating.

More detail on applications of IBAD is given in Chapter 16, this volume.

III. FILM FORMATION

A. Nonreactive Film Formation

In PVD, film formation and growth are determined by the nucleation of adatoms on a surface, and the parameter of nucleation density is important. A high nucleation density is generally desirable for good adhesion and a dense film. Nucleation density (and adatom surface mobility) is controlled by a number of factors including:

- Surface chemistry and chemical reactions
- Preferential nucleation sites
- Charge centers, steps, defects, grain boundaries
- Adsorbed species.

The nucleation density may be modified by

- Controlling the surface chemistry by cleaning or surface modification such as Al_2O_3 on Al
- Substrate heating
- Generation of nucleation sites, e.g., defects, steps
- Adsorption of reactive species, e.g., O (O_3) on oxides
- Concurrent energetic particle bombardment prior to and during deposition by introducing defects, recoil implantation of species, and physically implanting species.

B. Reactive Film Deposition

Reactive deposition of materials may be used to form compounds by reacting the depositing species with a codepositing reactive species or with an adsorbed reactive surface species to form a nonvolatile compound. For example, a mixture of Ti and C may not have any TiC, may be partially TiC and the rest unreacted Ti and C in solution, may be substoichiometric TiC_{1-x}, or may be TiC with excess Ti or C—all of which will have different properties. Generally, for low-temperature deposition, the best situation for reactive deposition is one in which one of the reaction species is condensible and the other is gaseous (e.g., Ti + N). If both species are condensible, the best deposition condition is to have a high substrate temperature to promote reaction or to use postdeposition heat treatment.

There are a number of techniques for performing reactive atomistic film deposition. The simplest way is to evaporate the material thermally in a partial pressure of a reactive gas (reactive evaporation). This generally gives poor quality films, because the materials are not completely reacted, and the high gas pressures result in gas-phase collisions and nucleation of the depositing material, giving a low density deposit.

In another general process, the gaseous reactive species may be "activated" by forming excited species, radicals, and ions in a plasma. The reactivity of the species can be increased by adding internal energy (excited species), by fragmenting the species to form radicals (uncharged species of O, N, F) or ions (charged species of O^+, O^-, N^+, Cu^+, Cu^{2+}), or by forming more reactive species (i.e., O_3 from O_2 + O). This is most often done in a plasma, in an arc, or by radiation absorption such as can be done with a mercury vapor lamp or an excimer laser. In the case of the activated species, the reaction probability with the adsorbed adatoms is increased over that of the molecular reactive species. Activated species may also be produced in a separate source to produce a reactive plasma beam or reactive ion beam.

Reactive deposition may be performed in a low- or high-pressure plasma or in a vacuum. In the absence of a good vacuum, gaseous species from the ambient impinge on the surface and adsorb to some degree. For an ambient pressure of 10^{-3} Torr, gaseous particles will impinge on the surface at about 10^3 monolayer (ML)/s (compared to a typical deposition rate of about 10 ML/s). The adsorption probability and adsorbed film thickness will depend on a number of factors such as the impinging species (i.e., plasma parameters), the nature of the surface, the adsorption sites, etc. For instance, it has been shown that atomic oxygen on silicon will adsorb with a higher probability and to a greater ML thickness than will molecular oxygen and that ozone is strongly adsorbed on Al_2O_3.

In the case of a plasma environment in which the species are activated, the adsorption may be higher than in an environment in which there is no activation, and this, in turn, influences surface reactions and recoil implantation into the surface. In vacuum, one expects adsorption to be low, and physical penetration of the bombarding species into the surface will be the more important effect. The effects of adsorption on reactive deposition have not been studied to any extent [1].

The composition of the reactively deposited material may be controlled by controlling the availability of the reactive species. This allows the gradation of composition from an elemental phase to the compound phase. For example, Ti to TiN to enhance adhesion of the deposited TiN material.

The reactivity can be further increased by using concurrent energetic particle bombardment either by the depositing/reacting species or by a species that does not enter into the reaction (inert ion bombardment). Generally these energetic species are obtained by charging (ionizing) a species and accelerating the ions in a electric field, but the energetic species may also be neutral, such as those formed by charge exchange processes or neutralization and reflection of energetic ions from surfaces. This bombardment enhances compound formation by introducing heat into the surface, adding kinetic energy to the adsorbed species, disassociating adsorbed molecular species ("surface activation"), producing secondary electrons that assist chemical reactions, and selectively desorbing or sputtering unreacted or weakly bound species. Concurrent bombardment effects can be enhanced by mixing a heavy inert gas with a light reactive gas to give bombardment by both species.

Periodic bombardment of a depositing species by an energetic reactive species can accomplish many of the same effects. For example, one can deposit several monolayers of aluminum, bombard them with energetic oxygen ions, and then deposit more aluminum, etc. This process has been termed alternating ion plating.

Concurrent energetic particle bombardment during atomistic film deposition has been shown to have a substantial effect on the composition, structure, and properties of compound films. In general, the bombardment allows

- Chemical reactions to occur at low substrate temperatures
- Formation of more stoichiometric materials
- Decreased incorporation of unreacted species
- Formation of higher density films
- Better surface coverage.

Plasma deposition environments may give a reactive deposition process that is not normally expected. For instance, the sputter deposition of gold on oxide surfaces in an oxygen-containing plasma gives rise to very adherent gold films by giving a high nucleation density, and recently this deposition condition has been shown to result in gold-oxygen bonds being formed, whereas gold oxide has only been formed previously by electrochemical techniques.

Reaction (rate and degree) of particles in contact with each other depends on a number of factors including the

- Degree of previous reaction
- Reactivity of the species (including "activation")
- Energetics of the reactive species (internal and kinetic)
- Concurrent ion bombardment (energetic, secondary electrons, resputtering)
- Temperature of the substrate
- Reactive species availability (adsorbed on surface or impinging)
- Residence time of reactive species
- Presence of free electrons near the surface.

The probability that an adsorbed species will react with a surface depends on the nature of the species and the degree of reaction that has already occurred at the surface. For instance, oxygen molecules will react with a pure aluminum film, but nitrogen molecules will not. The probability that the oxygen molecule will react with the aluminum decreases as the aluminum reacts with the oxygen molecules (i.e., the coverage increases). In the case of atomic oxygen, the reaction probability will decrease with coverage. In the case of atomic oxygen on silicon surfaces, the reaction probability decreases monotonically with coverage through several ML coverages. If the material can form a series of compounds (e.g., TiN, Ti_2N) the probability of reaction is further decreased as the degree of reaction increases and it will be more difficult to form the higher compound. In may cases, a reaction occurs first at active sites on the surface providing a nonhomogeneous growth (or etching) mode.

The degree of reaction of codepositing species depends on the availability of the species and the time of contact, as well as the reaction probability. Obviously, if the species are not available to react, the reaction will not proceed to the desired extent. This gives rise to the "loading factor" that means a relationship exists between the surface area for reaction (deposited film area) and the amount of reaction gas necessary. If one of these is changed, that will probably necessitate changing the other.

IV. HYDROGEN EFFECTS ON FILM GROWTH

Hydrogen seems to play a very unusual role in the growth of some materials. In the case of silicon deposition from the silane (SiH_4) precursor gas in chemical vapor deposition (CVD), the incomplete decomposition of the precursor results in the deposition of amorphous silicon that can contain more than 20 at. % hydrogen. The hydrogen prevents Si-Si bonding. The amorphous silicon seems to deposit much like a polymer, giving very good surface replication and low void density in film growth. The growth seems to be controlled by the adsorption of species formed in the plasma [2–4]. Other materials such as boron and carbon show similar growth of an amorphous phase when hydrogen is present.

In the case of carbon, a diamond ("diamond-like") structure may be grown in the presence of hydrogen. In this case, the C-H bond on the surface seems to stabilize a high temperature/pressure diamond structure of the carbon until the deposition of another C-H causes the desorption of the original hydrogen atom. These diamond films may then show properties approaching natural diamond and diamond grown under high pressure-high temperature conditions. A problem with this type of growth is that the surface is relatively rough compared to that of diamond films formed by ionized deposition techniques. These diamond (hydrogen) films have been grown by a number of techniques and under a variety of deposition conditions.

V. SURFACES IN PVD: RESEARCH AND ANALYTICAL INTERESTS

For studying the nucleation density of adatoms on a surface, methods and techniques that have been used include optical (and other radiation) extinction during deposition. X-ray photoelectron spectroscopy (XPS) signal extinction with deposition (a function of ML deposited), [illegible] function changes with deposition, and in situ transmission electron microscopy (TEM). [illegible] are needed on engineering systems in which the nucleation studies are combined with studies on surface chemistry, surface preparation, adhesion, and film properties. Other needed research includes studies of the

- Structure and properties of the material formed on the surface during deposition that later becomes the "interphase" material found in the interfacial region between the film and substrate [5]
- Concurrent and prior energetic particle bombardment on nucleation density of the adatoms
- Adsorption of reactive species on a surface, the effect of molecular species on adsorption, and the production of unique species in the plasma
- Concurrent bombardment on chemical bond formation at surfaces, the formation of substoichiometric reaction layers, and enhanced reaction completeness

- Concurrent bombardment on chemical reaction kinetics on surfaces including synergistic effects of energetic inert species and molecular reactive species, and effects of secondary electrons, coverage, dissociation, recoil implantation, and the ratio of bombarding species to depositing species

- Concurrent bombardment on crystal growth on surfaces and the relationship among surface adatom mobilities, crystallographic orientation, and defect formation.

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APPENDIX

"Surface Effects in Reactive Ion Plating" by D. M. Mattox.

ABSTRACT

Ion plating is a generic term for deposition processes (vacuum-based and plasma-based) in which concurrent or periodic energetic heavy particle bombardment during deposition is used to modify the composition, morphology, microstructure, and properties of the deposited material. The beneficial effects of controlled bombardment are well documented in reactive deposition (and etching) processes; however, the mechanisms involved and their relative importance are poorly defined and understood. This paper reviews some of the possible mechanisms important in reactive ion plating and how they may vary with deposition conditions. The complete text is given in Appl. Surf. Sci., 48/49, 540 (1991).

13. PARTICLE BOMBARDMENT EFFECTS ON THIN-FILM DEPOSITION: A REVIEW

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ABSTRACT

In many atomistic film deposition processes, concurrent energetic particle bombardment (ions, atoms, molecules, atom clusters) may occur inadvertently and uncontrollably or bombardment may be used to deliberately modify film properties. These energetic particles can arise from (i) the acceleration of charged particles, (ii) high-energy neutrals from reflection from bombarded surfaces, or (iii) charge exchange processes. Particle bombardment effects that can affect film formation and growth include (a) modifying the substrate surface (cleaning, defect formation), (b) momentum transfer processes in the surface region (sputtering, desorption, recoil implantation, defect formation), (c) addition of heat to the surface region, and (d) formation of secondary electrons that can affect chemical reactions. These in turn affect film properties such as adhesion, residual film stress, film morphology, density, grain size and orientation, surface coverage, pinhole density, and surface area. The understanding of these effects and how to use them advantageously is important to those utilizing processes where concurrent energetic particle bombardment is occurring or can be made to occur.

The complete article is published in J. Vac. Sci. Technol., A7(3), 1105-1114 (May/June 1989) (104 references).

14. SOL-GEL COATINGS FOR ENERGY-RELATED MATERIALS

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ABSTRACT

Through sol-gel processing, the full flexibility of solution chemistry can be exploited to make films with finely controlled compositional characteristics; no less important is the possibility of exploiting colloid and polymer physics in general ways to achieve desired film properties. The advantages, disadvantages, and applications of sol-gel films are discussed with an emphasis on those properties that are unique to sol-gel processing.

I. INTRODUCTION: A LOW-COST SOLAR CELL

O'Regan and Grätzel reported [1] in late October 1991 that they had succeeded in fabricating a photovoltaic cell based on commercially realistic technologies. One of the enabling technologies in their device is a sol-gel coating. Although this cell may not be the answer to mankind's energy problems, it serves to illustrate some of the advantages of sol-gel coatings.

The cell is based on a porous TiO_2 (anatase) coating impregnated with a charge-transfer dye, a ruthenium-pyridine complex. Electrical contact is made throughout the porous film by an iodide electrolyte. Solar photons are efficiently absorbed by the film—46% of the solar flux at all wavelengths is harvested—and their energy is converted, at efficiencies exceeding 80%, to electrons injected into the conduction band of the TiO_2 semiconductor. After the collected current was sent through test loads and back into the electrolyte to regenerate the dye, overall efficiencies between 7% and 12% were found, depending on illumination. The authors reported exceptional stability for their cell with respect to decomposition under constant use. Owing to the low cost of materials, they feel that practical applications are feasible.

The success of this solar cell derives from a high quantum efficiency for charge injection as well as the substantial overlap between the absorption spectrum of the dye and the solar spectrum. However, neither of these attributes could be exploited unless a sufficient amount of dye could be illuminated while maintaining electrical contact with both a semiconductor substrate and a regenerative electrolyte. Thus, the porosity of the titania film is a decisive advantage.

The film was deposited from a colloidal suspension of 10-nm TiO_2 particles prepared by the hydrolysis of titanium tetraisopropoxide. A "paint" of these particles was spread onto a conductive glass slide and allowed to dry into a 10-mm film. After lightly sintering the film at 450°C to ensure electrical contact, a high surface area semiconducting support resulted with pores large enough to accept dye molecules; the surface area of the cell was increased 780-fold!

Aside from the porosity, other factors contribute to the economic potential of the solar cell. The purity of the titania is important, and, through the purity of the liquid reagents, it is attained. The relatively low-tech method of film fabrication requires minimal investment in equipment, yet retains wide flexibility to coat large areas or complex shapes. The thermal treatment is low in energy cost in comparison with most ceramic processing. Finally, in addition to chemical control, the manufacturer has physical control of the film precursors—the colloid—and the way they are deposited, which allows optimization of the cell performance via porosity.

II. SOL-GEL FILMS: DEFINITION AND HISTORY

No universal definition of sol-gel film processing exists. Perhaps the most general qualification is any film deposited from a liquid phase. Although necessary, this qualification would be perceived to be too general by the current sol-gel community. Sol-gel films are defined largely by processing:

> "A sol-gel film is a coating or free-standing film that is formed from a sol through continuous stages of increasing concentration of a solid precursor."

This definition comes closest to modern usage [2]. Precipitations, such as common gold or silver metallizations on glass, are excluded because such a film grows essentially at final density from the substrate into the liquid. On the other hand, precipitates that form in the bulk liquid and are then concentrated on a surface by settling, electrophoresis, or evaporation form a true sol-gel film by the above definition. A schematic of the sol-gel processing field, of which films are only a part, is shown in Fig. 1.

Typically, the sol is a solution of polymeric species or a suspension of "oligomers" including, possibly, particles in the colloidal size range. The liquid carrier must be volatile or, at least, volatilizable through heat treatment. During deposition through states of increasing solids concentration, this sol might gel, as in bulk sol-gel processing, however, the gel state is often a fleeting transient that quickly empties of liquid. Nevertheless, the structures formed during this stage, with varying amounts of porosity, influence the structure of the final film.

By the above definition, printing and painting are sol-gel film processes. Thus, sol-gel films are easily the oldest surface modifications invented by man, dating back tens of thousands of years. The first modern sol-gel films, according to the early, definitive review by H. Schroeder [3] of Schott Glaswerke, were Langmuir-Blodgett (LB) monomolecular layers, which by 1935 had been developed to the point of making antireflection coatings. LB films are formed by the slow withdrawal of a substrate through a molecular surface layer that is lifted from the liquid surface onto the substrate; they continue to be developed as a means of depositing very thin, high-molecular-weight layers, and they are considered to be a research discipline in their own right, separate from mainstream sol-gel technology.

Schroeder reports that the first oxide films (SiO_2) were made in Germany shortly before World War II by spin coating silicic acid onto glass. During the War, this process was used industrially, presumably as optical coatings, but the first products did not appear on the market until 1953 [4]. Large-scale production of automotive mirrors coated by sol-gel techniques began in 1959. Original patents on the chemical basis of sol-gel oxide films were filed simultaneously by the Schott chemists [5] and by Levene and Thomas (Owens-Illinois, Inc.) in 1969 [6]; the process itself was known through German patents to Schott and Leitz as early as 1939 [7]. The early Schott workers nicknamed sol-gels "glass from the bottle" [4].

Dislich [8] predicts that the future of sol-gel processing will be based on its strengths: high compositional and homogeneity control at low temperatures. Sayer and Sreenivas favor sol-gel processing as a way to evaluate new compounds quickly and cheaply [9]. In comparison with vacuum and chemical vapor deposition (CVD) techniques, sol-gel coating is not equipment-intensive or directional. For optical applications, the ability to coat both sides of an element simultaneously is a potential advantage [3]. Indeed, for any given application, sol-gel films may offer unique advantages.

III. METHODS OF FABRICATION

Sayer and Sreenivas [9] classify all ceramic thin-film fabrication into physical techniques, including vacuum evaporation, sputtering, and ablation, and chemical techniques, such as CVD and sol-gel processing. Part of the flexibility of sol-gel processing is the option of using physical mechanisms in conjunction with chemical reactions to achieve a desired result. For example, it is now common to trap colloidal particles inside a fine sol-gel matrix to render a film antireflective [10] or colored [3]. This hybridization of chemical and physical aspects accounts for much of the recent explosion of interest in sol-gel films.

The first step in sol-gel film fabrication is to meter a well-defined quantity of sol uniformly over the substrate; this can be accomplished in several ways discussed below. Second, the liquid phase is allowed to dry; often the evaporation is spontaneous and nearly instantaneous. The film density is strongly affected by capillary forces at this stage. Finally, the film can be heated to remove traces of liquid, improve adhesion, crystallize, or sinter the material. The heating step is optional since, for many applications, the dry film emerging from the second stage is robust enough. Indeed, the ability to fabricate ceramic and organic films exclusively by room temperature processing may prove to be a great advantage for bioactive films.

Sol-gel processing is simple and economical, but, as Guglielmi points out [11], it remains largely empirical in practice: sol-gel science is a recent invention [2]. The outlook is bright. Since 1982, more than 500 papers have been published in scholarly journals on sol-gel films.

A. Dip Coating

Nothing could be simpler than dipping a component or piece into a sol and withdrawing it. Figure 2 shows a side view of the process. Historically the technique of choice for optical films, this typically low-tech process allows great flexibility in part size and shape with a minimal equipment investment. However, the simplicity of dip coating masks the complexity of the physics and chemistry behind it.

The coating of photographic film with a gelatinous emulsion motivated early studies of the hydrodynamic entrainment of a liquid film by a withdrawing body. The first correct treatment, by Landau and Levich [12], predicted that the entrained film thickness λ (Fig. 3) scales with the withdrawal velocity u_o as $u_o^{2/3}$ (in the absence of evaporation) assuming simple, Newtonian viscosity. Guglielmi [13] cites a number of authors who have reported behaviors ranging from $u_o^{2/3}$ down to $u_o^{0.1}$, demonstrating, perhaps, that viscosities are not always simple or that surface-tension gradients are sometimes important. In any case, the interplay of gravity, surface tension, and fluid viscosity determines the amount of liquid metered onto the surface in dip coating in contrast to slot and roller coating, in which the liquid volume is dispensed by externally controlled pressure (see below).

Most sol-gel coating is done with a volatile liquid, such as short-chain alcohols; dip coating is no exception. Evaporation during withdrawal gives rise to an astonishing phenomenon: the entrained film rapidly approaches a steady-state thickness profile for a constant withdrawal velocity. A signature of this process is the presence of a "drying line" above which little or no free liquid is observed and below which the entrained liquid film tapers smoothly to the reservoir. The recession rate of this drying line is a function of its height above the reservoir, and the entrained film will rapidly grow to a length at which the recession rate matches the withdrawal rate. Typically, withdrawal speeds are of the order of millimeters per second, and the drying line stabilizes at a height of a few millimeters.

The steady nature of dip coating with volatile solvents engenders optical studies of the process. In Fig. 4, Schroeder shows how interference fringes in the film can be used to assess coating uniformity [3]. Since 1988 [14], Hurd and coworkers have been developing imaging ellipsometry to assess coating uniformity, in which images of the steady-state film through an ellipsometer yield thickness and index maps. The index maps reveal a measure of the local solids concentration, while the thickness maps relate directly to the evaporation behavior. At the drying line, which represents a sharp edge in the evaporation and vapor diffusion problem, we have shown that the sol concentrates very rapidly because of the precipitous loss of solvent [15]. This accelerated evaporation sets an unavoidable time limit on the gelation, aggregation, polymerization, or other chemistries occurring in the film, as Fig. 3 illustrates.

Surface tensions are usually finely balanced during dip coating, as the liquid surface radius of curvature usually exceeds 1 km except in the gravitational meniscus region [16]; this point can be appreciated by the difference in scales for the measured profile h(x) in Fig. 5. Surface tension is such an overwhelmingly large force, however, that dramatic things can happen when this balance is upset. The dipping of solvent mixtures having differing volatilities can lead to surface-tension gradients when one component is depleted from the mixture by differential evaporation, as shown in Fig. 6. The resulting surface-driven flows produce extraordinarily high shear rates, of the order of 10^4/s, that can be used for film structure control via, for example, shear-induced ordering [17].

The uniformity of dip-coated films is surprisingly good, given the fact that the sol is self-metered. Vibrations and air currents are easily and necessarily avoided; "edge-bead thickening" appears to be unavoidable [11]; good wetting is a prerequisite; phase separation in multicomponent systems can be a problem [18].

B. Spin Coating

Because of the burgeoning microelectronics and magnetic disk industries, spin coating of sol-gel films may now be the most important fabrication technique. A sol is dispensed onto a stationary, nominally flat substrate, which is then accelerated rapidly to spin about an axis normal to the surface. A portion of the sol is ejected by centrifugal force. Emslie et al. [19] showed that, remarkably, the film thickness becomes uniform regardless of its initial distribution. Meyerhofer first considered evaporation in the process [20] and predicted that the film thickness should scale with the angular velocity Ω as $\Omega^{-1/2}$, a result confirmed recently by Lawrence [21]. However, the effects of nonNewtonian viscosity can alter this scaling [21]. Unlike dip coating, the distribution of sol occurs more rapidly than variations in sol properties from evaporation [11].

Shear rates in spin coating can be large enough (> 10^3/s) to effect structural changes in the film [22]. The refractive index of silica films deposited from polysilicate sols shows an increasing trend with Ω; intuitively consistent with the idea of shear-induced ordering, this phenomenon remains largely unexplained.

C. Electrophoresis

Possibly the only way to produce a uniform, conformal coating on complex shapes is to use electrophoretic deposition [23]. The part must be conductive, and the sol must contain contain charged species. The latter criterion can almost always be met by judicious use of emulsification or surfactancy. When the part is held in the sol at a moderate potential with respect to an inert counterelectrode and where the choice of positive or negative potential signs depends on the particle charge, the electric field causes the particles to migrate and adhere to the surface. Thus the film passes through states of increasing solids concentration. The coating can be built up to large thicknesses in comparison to dip and spin coating, but, if the particles are insulating, the coating itself will choke off the electric field.

A major advantage to electrophoretic coating is its self-healing nature. Pinholes are filled preferentially, owing to their high field strength. Similarly, edges and protruberances acquire greater thickness than flat areas. These attributes make electrophoresis attractive for microelectronic coatings [23].

D. Free-Standing Structures

A growing body of sol-gel literature deals with fibers and free- standing films of glass-forming oxides. The major part of the effort has centered in Japan, beginning in the early 1980s. While not strictly a part of surface modification, this phenomenology deserves mention because of its intrinsic interest and the many aspects of structure formation it shares with deposited films. In fact, the coating of wires and fibers has a closer resemblance to this section than to the foregoing sections.

Sol-gel fibers were first reported by Sakka and Kamiya [24] in 1982. They allowed an alkoxide solution nearly to gel, then touched a glass rod to the surface and pulled up. By a process called spinning, a long, uniform fiber was created that became a dense glass fiber after heating. Diameters of a few microns to tens or even hundreds of microns are possible. The amount of material metered into the fiber by the gravitational meniscus has, to this author's knowledge, not been treated, although it appears to be a straightforward extension of the Landau-Levich treatment for films [12].

The characteristic of spinnability has remained a mystery. Sakka and Kozuka showed [25] that spinnable sols remain Newtonian at high viscosities and that they contain long, polymeric species as opposed to compact particles.

The same Japanese group pioneered free-standing film formation. Reviews by Sakka and coworkers in 1984 [26] and 1988 [27] treat the phenomenology. Commonly called "sheets," free-standing films have been produced in three basic ways: sheets have been drawn from spinnable solutions using wire frames, they have been extruded through slots, and they have been coated onto substrates from which they could be separated. Typical films are tens of microns thick. Huling and Messing reported an interesting variation [28] in 1988 in which they spin coated camphor disks with various sol-gels and then allowed the camphor to sublime. After firing, they produced very thin sheets, down to 1-mm thick, of crystalline aluminosilicates.

E. Other Coating Methods

Traditional high-speed, continuous coating is accomplished by premetering the sol onto a moving substrate using slots and rollers. The extensive literature on this subject has been reviewed by Scriven [29]. Although not normally considered to be in the sol-gel domain, these techniques promise to gain in importance as industrial applications are found. A recent research example that crosses the boundary into recognizable sol-gel processing is the study of "doctor- blading" by Casanova et al. [30]. Also called tape casting, the doctor blade forms a variable slit opening through which the substrate travels and the sol is dispensed.

Although spray coating, painting, printing, and many other techniques fit the definition of sol-gel films adopted here, they fall beyond the scope of this paper.

IV. DRYING AND HEATING

As pointed out by Scherer [31], the removal of liquid from bulk sol-gels is particularly troublesome due to the tendency of gels to crack or warp under drying stresses. Thick films and multilayer films suffer essentially the same problems as bulk gels. Very thin films, such as those formed by dip-coating ($h < 0.2$ mm), tend to be below the critical thickness at which cracking occurs. In any event, capillary forces can dramatically influence the structure and porosity of sol- gel films.

A. Capillary Collapse

Stress arises as soon as a gel no longer "fits" inside its host liquid volume. In dip coating, for example, the rapid loss of liquid near the drying line creates menisci in the pores of the gel that set up tension in the liquid. The Young-Laplace equation shows that this pressure is inversely proportional to the radius of curvature of an adjacent meniscus [31]. Further evaporation is impeded by liquid transport through the gel to the gas-liquid interface, a regime called the "constant-rate period" by Scherer. For most materials, the reactive force to this tension, exerted by the interface on the gel, causes the network to collapse until a point at which the gel can collapse no longer. Surface pores then emerge from the liquid as it recedes into the gel; this period is called the "falling-rate period."

A sobering calculation shows that, if the pores in the film are comparable in size to the precursor particles, then the menisci give rise to tens or even hundreds of atmospheres of tensile pressure. Whether actual pressures exceed 100 atmospheres is debatable, given the range of applicability of the Young-Laplace equation and the (meta)stability of the overexpanded liquid [17]. Nevertheless, Brinker has shown that the film compacts to a density that is proportional to the particle size as a result of capillary collapse [22].

Tu and Drake [32] discuss the heat and mass transfer during a drying process without consideration of capillary phenomena. They propose that during the constant- and falling-rate periods—called the diffusion-limited regime in their paper—not only is the transport of liquid to the evaporating interface important but also the transport of heat. In very thin films (not explicitly defined by the authors), of course, thermal transport is not limiting.

B. Stresses and Multiple Coats

Schroeder [3] identifies three stresses that can develop in sol- gel films. Intrinsic stresses are typically tensile and arise from the tendency of gels to shrink as they dry. Adhesion stresses arise in this situation because the gel is pinned to a substrate. Finally, thermal stress is important for materials that aren't well matched in thermal expansion coefficients.

Thermal stress is often the limiting factor in the extent to which multiple coats can be deposited. Of particular interest in this arena is the use of multiple layers to create interference optics that might meet with high temperatures. Schroeder [3] cites titania on soda-lime glass as a good thermal match—the difference in thermal expansion coefficients is less than 30%—in which repeated coats are viable. Silica, on the other hand, is not easily multicoated because its difference in thermal expansion coefficient exceeds 90%. Bräutigam and coworkers [33] have only been successful with silica using a full thermal treatment between layers.

The measurements of stress in sol-gel films is a science in its infancy. Schroeder used the deflection of a thin disk coated on one side to study titania films [3]. Cerqua and Hayden have applied modulated transmission ellipsometry [34] to assess residual stress as a function of various processing parameters. They found that even compressive stresses are possible depending on the age (extent of aggregation/polymerization) of the sol.

V. COMPLEX COMPOSITIONS

Although a large number of possibilities exist for single-component sol-gel films, multicomponent formulations offer even more numerous possibilities. A few examples are cited, but special applications, such as ferroelectric and superconducting films, will be treated separately in Section VI.

Colloidal inclusions have already been noted [3,10] as a means to modify optical properties. The use of metal and semimetal colloids or clusters remains a promising route, especially in view of recent activity with quantum-size effects in silicon.

Molecular mixtures can have equally profound optical and electronic effects. Cobalt oxide [3] was a pigment used in early research, and mixtures of titania and silica were used industrially [4] to adjust the refractive index. Cadmium stannate films were synthesized as a transparent semiconductor in initial research work.

The greatest effort appears to have gone into glass ceramic films. Dislich and Hinz [4] reported an eight-component formulation in their seminal patent [5]. An example of the extremely wide range of compositions possible by sol-gel processing is given by Puyané and González-Oliver [35], who studied binary, ternary, and quaternary oxides of silicon, titanium, aluminum, tin, indium, germanium, yttrium, and zirconium.

VI. APPLICATIONS

A. Electronic

There has been an explosion of papers in sol-gel processing of superconducting ceramics over the past few years, especially in Japan. The YBCO phase has been formulated [36], and Sakka's group has recently gotten involved [37]. Although reasonable critical currents (e.g., 13,000 A/cm^2) have been obtained, the quality of sol-gel processed films lags behind films prepared using physical deposition. Nevertheless, the ease and simplicity of the sol-gel process lends itself well to a wide range of stoichiometries [38].

Ferroelectric films of the lead titanate family are under investigation in a number of laboratories using sol-gel technology. Phase purity is a recurring problem, as the lead-poor pyrochlore phase tends to form at low temperatures. Uhlmann and coworkers have compared these sol-gel developments, including barium and strontium titanates, to physically deposited films [39]. In general, finer stoichiometric control was possible with sol-gel as compared to sputtering, but microstructural characterization is lacking.

B. Abrasion and Wear Resistance; Strengthening

Schroeder [3] relates a curious fact: The wear and abrasion resistance of a part can be enhanced by a sol-gel coating but only if the coating is very thin (a few nanometers). A similar observation was made recently by Maddalena et al. [40], who found that the strength of soda-lime glass rods could be enhanced by thin silica coatings. In fact, they found that, if the coating is too thick ($h > 0.2$ mm), the strength of the rod decreases. Apparently the well-known smoothing action of conformal sol-gel coatings works to repair surface defects that might otherwise nucleate a crack or abrasion.

C. Membranes

Ceramic membranes find application in food, chemical, and pharmaceutical separations for gases, liquids, and molten metals. Recently, membranes have been developed through sol-gel processing [41]. The sol-gel advantage is the control over porosity one has by controlling the size and ramification of precursors. The inclusion of zeolites in a dense sol-gel matrix provides a second route toward well-defined pores, as reported by Bein and coworkers [42].

D. Solar

Solar applications have been focused on the economical preparation of solar mirrors [43], except for the photovoltaic cell example described in Section I [1]. Coatings have been used to convert optically rough surfaces into flatter and smoother ones for later coating with a reflective layer [44]. Similar coatings have been used as protective films on solar mirrors [45] and as antireflective films [46].

VII. CONCLUSIONS

Surface modification by sol-gel films is a growing area of research for several good reasons. Sol-gel processing provides the flexibility and stoichiometric accuracy of solution chemistry while requiring relatively little or no heating and minimal capital equipment. The high cost of pure liquid reagents usually is not important in making thin films, but the necessity to filter reagents in critical applications could become a limitation.

No attempt was made to provide a comprehensive review. Rather, the examples were chosen to be illustrative. To those authors whose work was left unmentioned, the author extends his apologies in advance.

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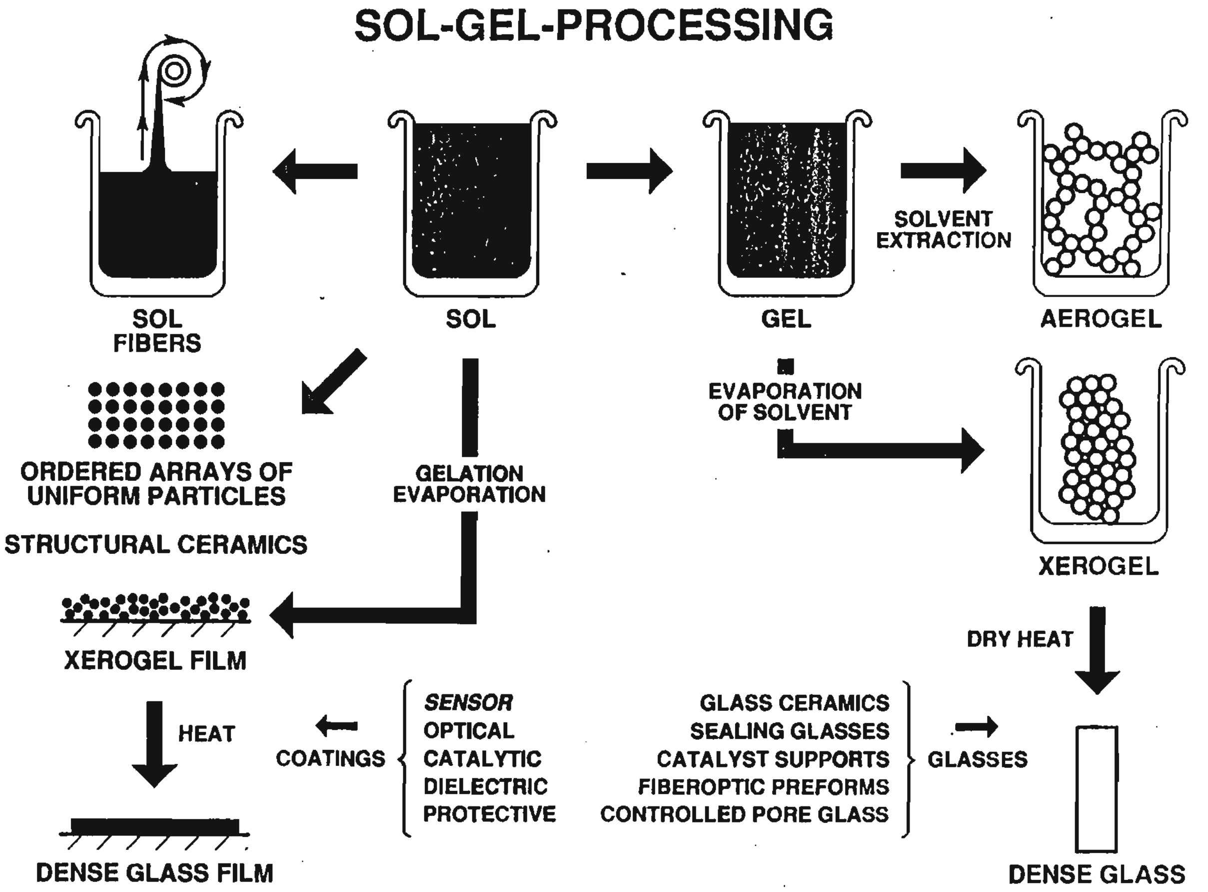

Figure 1. Sol-gel processing road map (courtesy of Jeff Brinker). Film formation is one possible branch; porous (xerogel) films have wide application even when only lightly heat-treated.

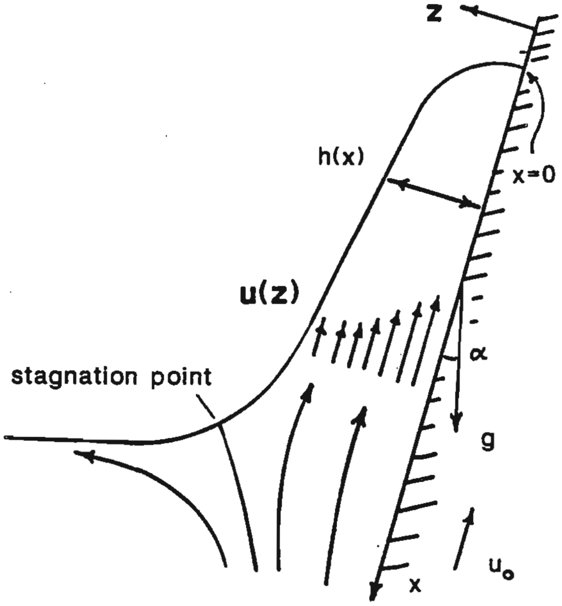

Figure 2. Dip-coating schematic. In general, the substrate can be inclined at an angle a in order to vary the amount of gravitational draining. Above the "stagnation point" all streamlines, and therefore all solids, are entrained. The "drying line" is defined as x = 0.

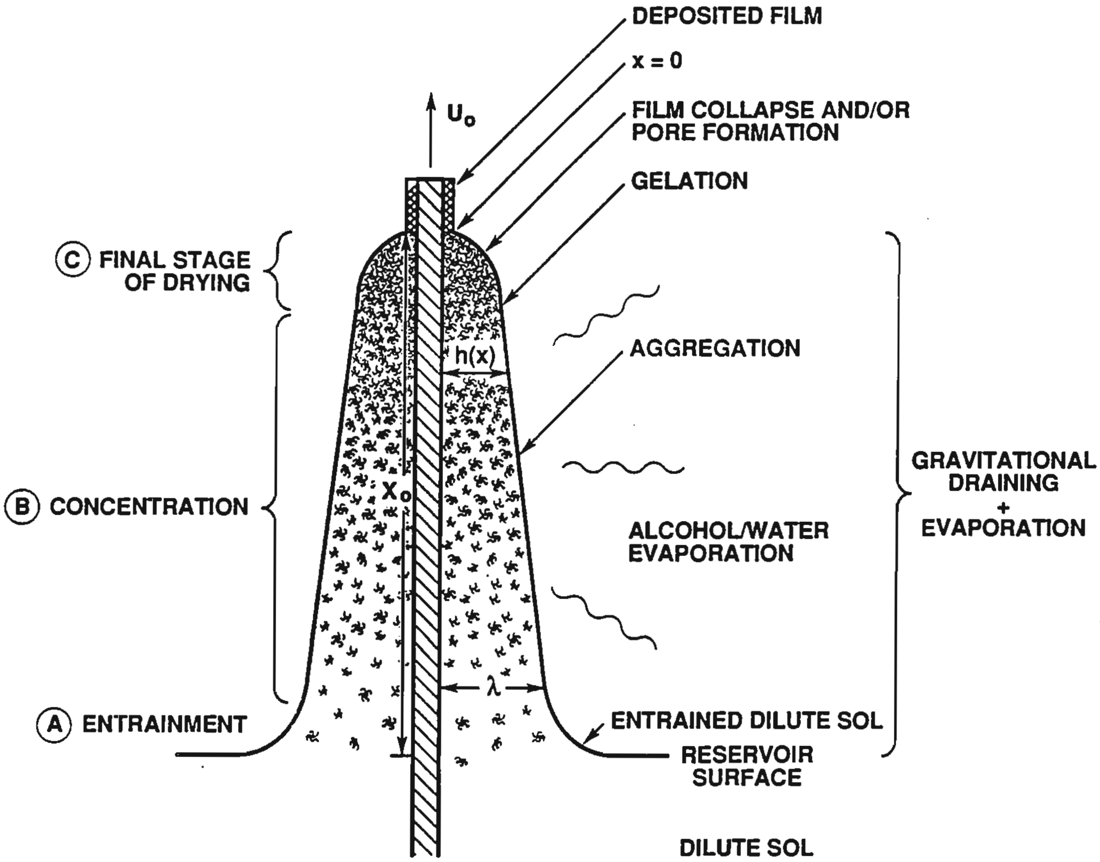

Figure 3. Stages of film formation in dip coating. In other types of coatings, many of these same stages occur, but not simultaneously.

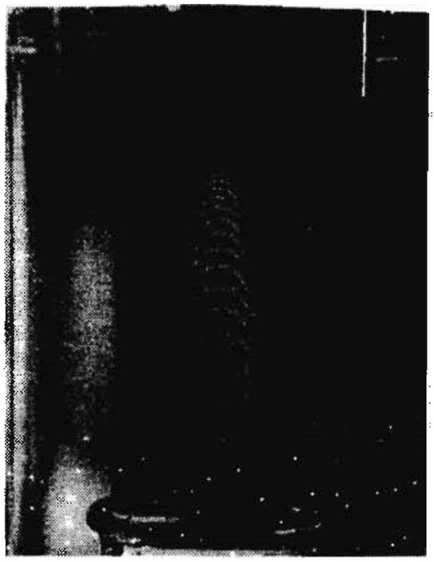

Figure 4. Interference fringes in an entrained film of ethanol being drawn from a beaker (bottom). The height of the film is a few centimeters.

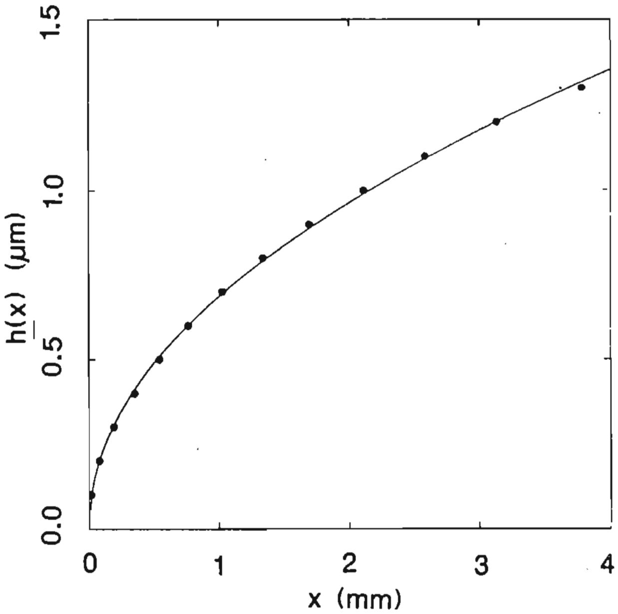

Figure 5. Thickness profile of dip-coating film of pure alcohol. The parabolic shape is a consequence of evaporation effects.

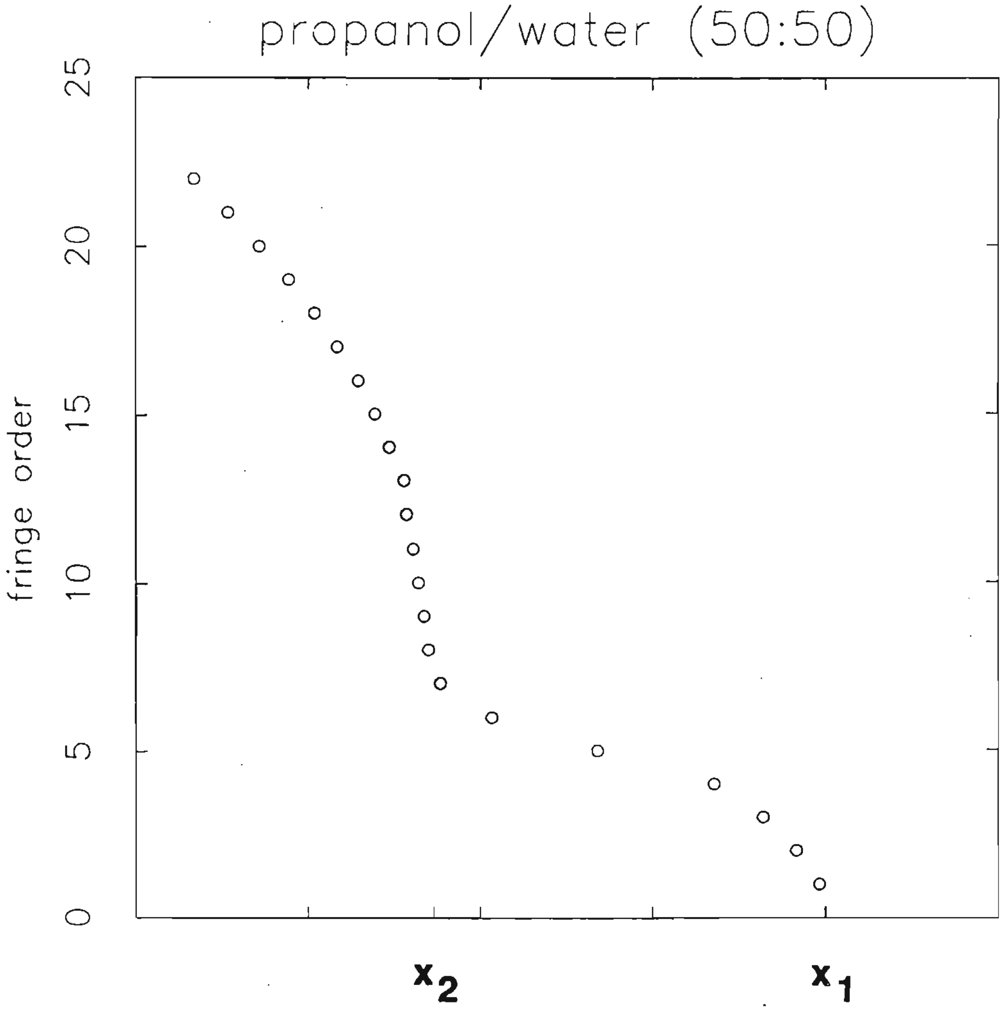

Figure 6. Thickness profile of a propanol/water mixture. The more volatile alcohol is essentially completely evaporated by $x = x_2$, while the water lasts until x_1.

15. HIGH-ENERGY ION IMPLANTATION OF MATERIALS

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ABSTRACT

High-energy ion implantation is a very flexible type of surface treatment technique, because it offers the possibility of treating almost any type of target material or product with ions of almost any chemical species or combinations of chemical species. In addition, ion implantations can be combined with variations in temperature during or after ion implantation. As a result, the possibility of approaching a wide variety of surface-related material problems exists with ion implantation. This paper will outline factors pertinent to the application of high-energy ion implantation to surface engineering problems. These factors include fundamental advantages and limitations, economic considerations, present and future equipment, and aspects of materials science.

I. INTRODUCTION

This paper will emphasize the technique of simple, direct high-energy ion bombardment of materials for improvement or tailoring of near-surface properties. The energy range of interest is from about 25 keV to about 400 keV. Thus, the technique can be contrasted with lower energy processing techniques such as ion plating, chemical vapor deposition (CVD), or ion nitriding. The related, but more complex, technique of high-energy ion beam assisted deposition (IBAD) will be treated in a separate paper [1].

Development of high-energy ion implantation can be credited partly to the early nuclear industry, in which ion production, acceleration, and mass separation were expanded into a sizable technology for isotopes separation. From the materials science standpoint, ionization of the atoms per se usually plays little to no role in the practical outcome, in comparison with, hypothetically, bombardment with fast neutral atoms of the same energy. Ionization facilitates acceleration, mass separation, and dosimetry for the bombarding ions.

Ion implantation is currently most widely used in the solid state electronics industry, in which the technique is used for introduction of dopants in carefully controlled quantities into elements of integrated circuits. Over 1000 ion implanters are in use for this purpose in the economically advanced nations. In part because of this success, research is now directed toward the constructive modification of practically every surface-related property in all classes of materials using high-energy ion bombardment. Goals include the construction of insulating layers on (or buried in) conductors and semiconductors; the construction of conducting layers on (or buried in) insulators; the modification of virtually all possible surface optical properties; improvements in corrosion, catalysis, or other electrochemical properties; improvements in wear and brittle failure; and fabrication of thin single-crystal films of artificial diamond, for example. Moreover, there are already a few other commercial successes for ion implantation, besides solid state electronics. These are mostly in the areas of biomedical materials, aerospace and defense materials, and certain production tooling.

In the following sections of this chapter, factors pertaining to the use of direct ion implantation for surface engineering of materials will be identified and discussed. Examples of materials science results, applications, and possible applications will be given.

II. FUNDAMENTAL ASPECTS

As far as particle-solid interactions are concerned, there are four important issues to consider for any experiment or process design. Fortunately, the applicable physics is now rather advanced, and results can be predicted with fair to good accuracy with quick, easy-to-use computer codes. The most widely used code is TRIM [2], which is available for personal computers free of charge.

A. Range and Energy of Energetic Atoms

When energetic atoms penetrate into a solid, much of the energy loss is caused by elastic collisions with target atoms of the solid. As a result, atoms in a beam, incident at a given energy, are statistically scattered laterally and longitudinally as they slow down. The resulting depth distribution over which the implanted atoms come to rest is typically somewhat Gaussian in form, but the distribution may also be skewed, depending on beam and target parameters. Figure 1 shows a typical ion implantation distribution for ions incident at a single energy, compared with a TRIM calculation.

B. Radiation Damage

Because of the atomic collisions involved in the slowing process, many target atoms (typically about 1000 atoms per incident ion) are displaced from their normal lattice sites in the target material. This large energy deposition in the product is a unique aspect of high-energy ion implantation as a materials processing technique. The process is called radiation damage because target atoms are displaced. In fact, the results are as often beneficial as they are deleterious. The damage can result in homogenization, refinement of microstructures, improved adhesion of ion-treated layers, and amorphization. Numbers of displaced atoms are also calculable by TRIM. Ultimately, most of the vacancies and interstitials recombine to produce considerable healing.

C. Sputtering

Sputtering is another aspect of radiation damage in which knocked-on atoms near the surface are ejected from the surface. Sputtering yields (Y) are typically 0.2 to 10.0 target atoms per incident ion, depending on beam/target parameters. Thus, there is often no net addition of material to a target due to ion implantation, and many times there will be a net loss. One effect of sputtering is to limit the concentration of the dopant that can be introduced by ion implantation. Because of erosion, the outer surface is a moving interface that moves into the previously implanted volume. The resulting maximum concentration of the dopant at saturation at the surface is about 1/Y. Other aspects of sputtering include angular dependence of sputtering from each element of topography on the surface, angular dependence for shaped products in ion beams, and dependence on crystallite orientation. Distinctive surface textures can result from combinations of these factors (Fig. 2).

D. Heat

The high energy of the process eventually appears as by-product heat deposited directly in the target. One of the frequently claimed advantages of ion implantation is that it is a low-temperature process. The claim is true, because heat is not needed to achieve penetration. By-product heat must be managed, however. This is usually achievable by some combination of cooling and rate control for the implantation. Ion implantations can be performed over a range of temperatures from cryogenic to quite high values, depending on product requirements.

III. GENERAL ARGUMENTS

A. High Energy, Chemical Flexibility, and Metastable States

Ultimately, the more impactive contributions of ion implantation may result from the fact that, in principle, the high energy of the process means that almost any chemical species can be injected into almost any target—plastic, metallic, ceramic, or semiconducting—regardless of ordinary chemical reactivity. This means that a large variety of presently unknown metastable states, with potentially beneficial properties, could be created by ion implantation. Radiation damage also causes or aids in producing metastabilities, e.g., amorphization of many materials. Moreover, known chemical reactions can be employed in new and creative ways by using ion implantation. Buried, insulating oxide layers such as Si and Al are examples (ion implantation of oxygen). Reactive ion etching or polishing (ion implantation of F or Cl) is another. Together with temperature variation during and after processing, ion implantation allows a wider range of parameterization than is possible with most other types of surface treatments. A disadvantage is that considerable R&D is often required for development of a single product or process. Predicting engineering performance in advance of testing is difficult. Therefore, rapid economic advancement is not necessarily assured.

B. Thickness of Ion Treated Layers

The depths of ion treated layers in solid materials are generally less than 1 μm (Fig. 1). This is typically only about 10% of the depth of various coatings that are in competition for wear and corrosion protection. Thus, mechanical fragility is a possible problem, and perhaps to a greater extent, a perceived problem in the marketing of ion implantation products and services. Actually, ion implanted layers can be more rugged than many suspect. For certain applications such as pure corrosion protection, without too much mechanical stress, ion implantation is more effective than many coatings because of extremely good lateral uniformity. In particular, this means the absence of pores where corrosion events can nucleate. For cases in which ion implantation has won markets in improved production tooling, tolerance has often been the key factor, together with difficulty in hardening the tool by competitive methods without loss of tolerance. Clearly ion implantation will nearly always be one of the last steps in the manufacture of any product to which it is applied.

C. Cost

High cost is a major disadvantage of ion implantation if treatment of large areas is contemplated. Consider an ion dose of $3 \times 10^{17}/cm^2$, which is typical of what might be needed for corrosion protection or wear improvement of a metal product. The lowest cost that could be projected for processing materials to that dose in the United States is perhaps about $\$400/m^2$, with single modules of equipment of the type described below. This estimate already takes into account some possible economies of scale. Further improvement in costs may result from future equipment developments (see below), and very large scaling could presumably reduce costs a great deal. At present, ion implantation costs can be born by products such as nuclear fuel clad, hip joints, or other specialty products of high value. Even some industrial tools can bear such costs, but many products cannot. For large areas, costs per unit area will be approximately linear with dose. One avenue to cost reduction might be more optimal designs from the materials science standpoint, which might result in important dose reductions.

D. Environmental Factors

Ion implantation is regarded as one of the most, if not the most, environmentally acceptable surface treatments. One reason is that the process achieves excellent economy in use of feed material because of very effective application. For the dose of $3 \times 10^{17}/cm^2$ mentioned above (a rather high dose), about 1 lb of Cr would be required to treat 1 acre of surface, or about 3.7 lb of the precious metal Ir would be required for the same number of Ir atoms as for 1 lb of Cr. Process discharges are correspondingly small and generally benign.

E. Other Factors

It is nearly impossible for an ion treated layer to spall from a surface. This feature is of possible importance for performance, environmental, and safety reasons. Very precise dosimetry is possible, as in semiconductor doping, for example. Often there is no change in the appearance of a surface due to ion implantation. This has been both an advantage and a disadvantage, depending on the application.

IV. EQUIPMENT

A. Present Equipment

There are currently five types of commercial ion implantation equipment available. Concepts, intended purposes, advantages, and disadvantages will be presented. Four of the implanters are ion beam devices, but one is a plasma device that involves different concepts.

1. Magnetically Analyzed Plus Postacceleration Ion Beam Implanter

This type of ion implanter, having emerged as the industry standard for solid state electronics, is by far the most widely used at present. Therefore, it provides a logical reference point for discussing competitive features. Figure 3 is a schematic layout of such an implanter. The ion source part of the implanter is usually a type of plasma source known as a Freeman source, but such a source may also be modified to allow for sputter ejection of ions into the plasma. By using such a source in conjunction with suitable recipes, ions of most chemical species can be generated. Ions from the source pass through an extraction/preacceleration stage, which brings the beam up to about 30 keV for magnetic analysis. The magnetic analysis stage reduces the beam to a single charge state of a single element (and generally a single isotope of that element), that is delivered to the mass analyzing slit. Thereafter, the beam is further accelerated in the postacceleration stage up to an accelerator potential of about 200 kV. If the charge state is 2 instead of 1, the particle energy will be doubled (e.g., 400 keV instead of 200 keV). Typically there is a large sacrifice in beam intensity to achieve charge states higher than 1. After the beam passes through the accelerating column, beam optical devices allow delivery and rastering of the beam to sizable targets in the vacuum end station, as desired.

The ion implanter of the type shown in Fig. 3 provides several advantages but also provides the most expensive process of any of the implanters. The ion source, in conjunction with the magnetic analysis, provides the most chemical flexibility. The device provides the best overall quality control, including beam uniformity and dosimetry (on a flat area). Because of the two acceleration stages, a wider energy range is provided than is usually found on competing implanters. Currents (of about 10 mA) are lower than for the other implanters. In addition to use in the solid state electronics industry, this type of implanter has found general use. A disadvantage of all beam implanters is that shaped (not flat) surfaces must be manipulated in the beam to achieve uniform doses. A variety of fixturing devices are available to perform these operations in vacuum.

2. Unanalyzed Beam Gas Ion Implanters

Because of the costs associated with the analyzed beam process, a simplified design has been developed that is known as the unanalyzed, broad beam gas ion implanter (Figs. 4 and 5). This type of equipment is intended primarily for implanting metallurgical products with nitrogen ions for corrosion inhibition, wear inhibition, etc. Such an implanter can make use of more than one type of ion source, and very large currents are possible. Capabilities of the sources themselves are not necessarily different from those of analyzed beam implanters. But because ions of all constituents in the feed recipe are delivered to the product, the chemical quality of the beam depends only on the purity of the feed material. Thus, if a metal ion plasma were volatilized by use of a chlorination recipe, Cl ions would also be delivered to the target. For this reason, unanalyzed beam implanters are regarded as most suitable for ions that can be generated from pure gaseous material such as N. If there were sufficient reasons, inert gases could also be used, and hydrogen-containing gases (methane, silane) could be used if the hydrogen were not a problem to the product. Capabilities of such implanters are as much as 100 mA at 100 keV. Without magnetic analysis, such an implanter delivers both multiple ionization states (e.g., N^+ and N^{++}) and singly ionized atomic and molecular states (e.g., N^+ and N_2^+). Given that the accelerator potential is fixed, either effect amounts to particle energy dispersion, and therefore range dispersion, for delivered N atoms. The molecular effect is the larger of the two for ion sources used in these implanters. For metallurgical purposes, dispersion, instead of the more highly peaked implant distribution (Fig. 1), is often not a disadvantage. Accurate dosimetry may be compromised.

It can be argued that an ultimate advantage to this big beam type of technology, compared with plasmas that require magnetic confinement (see Section IV.A.5.), is "scalability." This means that for sufficiently large single modular targets, or for a sufficiently large total area treatment rate, economies of scale are available for this technology, whereas for magnetically confined plasmas, even low energy ones, scaling up to areas above a certain optimum may become quite costly.

3. Analyzed Beam Gas Ion Implanters

If silicon wafers (held at high temperatures) are bombarded with high energy O ions to very high doses, the O precipitates as an insulating layer of SiO_2 in the subsurface of the Si, and the single-crystal Si is retained at the surface on top of the insulating layer. This fact has given rise to advances in silicon-on-insulator technology. In commercial application, the technique is known as the SIMOX process. For execution of the process, good control of range and dosimetry is needed. Eaton Corporation has developed a system for performance of the process. In concept, the layout is similar to that of Fig. 3, because magnetic analysis is provided. Single atoms of O at single values of energy can be delivered. The present system delivers 85 mA at 180 keV, but expansion in capability is said to be imminent. Presumably such a system could be adapted for use with other gases if a process were needed.

4. The Metal Vapor Vacuum Arc (MEVVA) Technology

The MEVVA technology makes use of a vacuum arc ion source to generate high ion currents of metallic materials [4]. No gaseous plasmas are used in the source, and the only feed material needed is solid metal of the desired species. Thus, the source provides excellent vacuum quality for the target without using extensive differential pumping. The source generates metal ions with a range of ionization states (but no molecular states), and the beam is delivered unanalyzed. Therefore, pertinent remarks given above apply. The principle advantage of the system is economy in the ion implantation of metallic species. The system is complementary in capability to the unanalyzed gas ion implantation system described above. The beam is simply a cone diverging from the source, also. The source is, in fact, a rapidly pulsed source. At present, the time-averaged capability is about 50 mA of current at 100 keV of accelerator potential.

5. The Pulsed Source Ion Implantation (PSII) Technology

The pulsed source ion implantation (PSII) technology [5] is the only currently existing high-energy system that is not a beam implanter. Thus, the ions are not in free flight when they impinge on the target. Instead, the product is a field terminal in the process. This technology is a derivative of fusion energy technology. Ions in a large plasma, generated by electron cyclotron resonance (ECR) microwave or other means, are extracted directly to the target (product) by a pulsed, high-voltage supply. Arcing to the surface is prevented by the pulsing. This technology is the most competitive with the unanalyzed gas ion type of implanter. As with that technology, the PSII technology is intended primarily for use with gas ions, particularly N, but its use with other gases is also possible. Hybridization or combination with other coating techniques to achieve ion assisted deposition is also possible. The constitution of the ions delivered is about the same as for the unanalyzed beam, in terms of molecular and ionization states. The most important advantage of the system is cost, and this advantage results in good part from the fact that the ions are incident at normal angles to essentially each surface element of the product. This means that manipulation of shaped products is not needed to achieve uniform treatment. Also, if sputtering presents a concentration limitation for beams, that concentration limit will be higher for normal incidence. Clearly there will be some loss of flexibility for treatment of insulators, because such products would at least require backing conductors of approximately the same shape.

B. Future Equipment

Ion beam processing equipment for the 21st century is being developed most intensively in Japan. A good fraction of the effort is under the auspices of a major joint government-industry initiative, and the corresponding agency is known as the Advanced Material-Processing and Machining Technology Research Association (AMMTRA). In addition to ion beam technologies, laser and other advanced materials processing technologies are being developed. The government contribution to the ion beam technologies is said to be more than $100M. In addition to equipment development, materials science research is also being supported. Competing industries, which are not a part of AMMTRA, are quite active also.

Table 1 summarizes the programs of AMMTRA in the area of ion beams [6]. Figure 6 is an illustration of the sheet ion system being developed by ULVAC Japan, Ltd. Such a system will be capable of processing very large surface areas.

V. MATERIALS SCIENCE

Each problem that arises will likely require a specifically selected R&D approach and then a correspondingly specific process design. The following general remarks and illustrations are intended to provide ideas as to what might be possible.

A. Amorphization

Ion bombardment results in amorphization of certain materials whose chemical makeup lends a susceptibility towards amorphization. If this chemical predilection exists, amorphization results from radiation damage alone and usually occurs at a rather small dose. Therefore, amorphization will usually be quite inexpensive in any case in which it can be projected as having a practical benefit. If the target does not have the suitable initial chemical character, it might be produced by high-dose ion bombardment. Then amorphization should soon occur. This latter pathway will generally be more expensive, however.

Table 1. Summary of AMMTRA R&D Projects [6]

Subject	Main Issue of Development	Target Specifications	
		Mid (FY 1990)	Fin (FY 1993)
Development of high-current metal ion beam system [Nissin Electric Co., Ltd.]	(1) High-current metal ion source and ion transport	Metal ion	Al, Si$^+$ 100 eV-100 keV 100 mA (100 keV)
	(2) Ion beam technologies for surface modification	100 keV (Al$^+$)	Modification area $\geq$ 100 cm^2 Current density 1 mA/cm^2
Integrated, high-current ion beam system [ULVAC Japan, Ltd.]	(1) High-energy, high-current ion beam system	Sheet ion beam 100 keV, 250 mA	Sheet ion beam 100 keV, 2A
	(2) Low-energy ion beam system	Low-energy ion beam $\leq$ 100 eV, 1 mA	Low-energy ion beam $\leq$ 100 eV, 5 mA
	(3) In situ beam diagnostics		
Ionized multiple beams technology with high deposition rate [Mitsubishi Electric Corporation]	(1) Cluster source with high deposition rate	200 mm diameter 0.3 μm/min	Al, Bi, Sr, Ca, Cu ion beams
	(2) Uniform ion current density on wide substrate		
	(3) Excited gas source with high flux		200-mm diameter
	(4) Compact designing of ionized cluster beam (ICB) source and gas source		0.1 mm/min
High-current focused gas-phase ion beam system [JEOL, Ltd.]	(1) Gas-phase ion source	He$^+$	He$^+$ ion beam Beam diameter $\leq$ 10 nm
	(2) He gas recondenser	2 μA/sr	2 μA/sr
	(3) Focusing column for gas phase ion source (GPIS)	$\leq$ 20 K	25 pA
	(4) Microlithography system	$\leq 2.66 \times 10^{-7}$ Pa	100 keV
High-energy ion beam system [Hitachi Ltd.]	(1) Variable-frequency radio frequency quadrupole (RFQ)	$\geq$ 1 MeV $\geq$ 0.5 mA (pulse)	0.5-4.0 MeV (variable) $\geq$ 1 mA
	(2) Microwave ion source for multiply charged ion beam		
	(3) MeV ion implanter		

Table 1. Summary of AMMTRA R&D Projects [6] (Concluded)

Subject	Main Issue of Development	Target Specifications	
		Mid (FY 1990)	Fin (FY 1993)
Surface improvement technology by ion implantation [Nippon Sheet Glass Co., Ltd.]	(1) Improvement of glass surface (2) Evaluation of improved glass	Improvement time = 1 h Glass substrate ☐ 50 mm	Improvement time ≤ 10 min Glass substrate ☐ 300 mm
Modification of metal by ion implantation [Kobe Steel Ltd.]	(1) Improvement of corrosion resistance of Ti and carbon steel (2) Improvement of wear resistance and surface hardness	Evaluation of mini-sized sample	General corrosion rate ≤ 0.125 mm/yr Vicker's hardness ≥ 1000
Deposition of high-reflection X-ray mirror [Japan Aviation Electronics Industries, Ltd.]	(1) Design of optical systems (2) Ion beam sputter deposition (3) Ion beam deposition	Reflection ≥ 20% Incident angle ≥ 5°, λ = 1-30 nm 25-mm diameter	Reflection ≥ 20% Incident angle ≥ 5°, λ = 1-30 nm (100 mm × 100 mm)

The following chemical and other factors favor amorphization from the empirical point of view.

- Chemical bonding (in order)—covalent, ionic, metallic
- Complex equilibrium structure for the chemical composition at the bombardment condition
- Narrow compositional range for equilibrium phase field (e.g., intermetallic "line" compounds)
- More elements
- Two or more phases of differing crystal structure in chemical equilibrium at the bombardment temperature
- Low melting point
- Low-temperature bombardment.

Because bombardment temperature is a factor, a design choice as to whether to produce amorphization or not during ion implantation can sometimes be made. Amorphization can have varying effects. Ironically it can reduce brittle effects, provide isotropic deformation modes, improve fracture strength, and reduce the elastic modulus for ceramic materials, but it seems to make metallic materials more glassy.

B. Effects in Polymers

At low doses, ion bombardment produces increased cross-linking, increased polymerization, and increased ultraviolet (UV) absorption [7]. At higher doses, hydrogen gas evolution, densification, and finally carbonization occur. Beam pyrolysis of photoresists painted onto metal surfaces can result in hard carbon coatings with excellent adhesion and properties [8].

C. Semiconductors

In addition to the doping and SIMOX process already mentioned, it is possible to produce a subsurface layer of cobalt silicide, which is fully metallic in conducting qualities [9]. Considerable research continues in compound semiconductors such as SiC, CdTe, and GaAs for which amorphization and epitaxial regrowth are special problems in comparison with Si. Ion implantation doping for solar cell production has been considered, and a non-mass-analyzed system for ion implantation of P, using solid metal feed material, was designed and evaluated [10]. The process is claimed to be economical and environmentally benign.

D. Metallic Materials

A variety of surface engineering approaches are possible, depending on problem details and economic factors. Simple nitrogen ion implantation often has very favorable effects on wear and fatigue of metals and alloys high in Cr, Ti, or Al. Nitrogen implantation usually does not result in improvement in friction. Treatments that result in carbonaceous or carbide coatings are possible. Figure 7 illustrates one successful case of salt-pitting corrosion protection for an aluminum alloy pillow block material for helicopters [11]. The application actually involved fretting corrosion. Fretting is considered to be a particularly favorable type of wear problem for approach by ion implantation because spalling is so difficult. The dopant that worked was Cr. Nitrogen ion implantation produces large increases in the electrochemical salt pitting potential for aluminum, but corresponding increases in salt spray performance were not observed, as they were for Cr.

E. Ceramics [12]

Certain effects due to amorphization were identified above. Figure 8 is a Weibull analysis for engineering fracture stress of Al_2O_3. Two types of ion implantation have been done. In the first, a high dose of Cr was used at room temperature. In the second, a low dose was used at temperatures at which amorphization occurred. For Al_2O_3, an implantation at 77 K was required to produce amorphization, but for ceramics that are amorphizable at room temperature, the amorphization process would be quite economical. For the amorphous case, the stress increases by a factor of nine for extrapolation to the cumulative failure level of 0.2%. In addition, amorphization of ceramics might produce a variety of other benefits. Projected Hertzian stresses and stress concentrations arising in tribological situations might be reduced due to amorphization. Elastic and plastic compliance for adhesion to dissimilar materials might be improved.

For high-dose implantations, metallic dopants precipitate as metal particles in an Al_2O_3 matrix provided that the postimplantation anneal is done in vacuum. For annealing in oxidizing atmospheres, metallic dopants are incorporated as oxide alloys. Buried conducting thin-metallic layers, analogous to the planar buried conducting or insulating layers formed in silicon by ion implantation, have not been formed in sapphire.

Low-dose ion implantations in graphitic and glassy carbon produce dramatic improvements in wear [13].

VI. SUMMARY

On its pure technical merits, the surface processing technique of high-energy ion implantation would appear to offer good prospects for improving technologies that will be applied in the future in the transportation and utilities industries. The problem areas that seem most suitable for approach by ion implantation include interfaces of dissimilar materials (metal-polymer or metal-ceramic interfaces), corrosion and tribology in general and certain problems pertaining to ceramics (fracture, spalling of bearings, etc.). For the near future, however, the high cost of ion implantation is likely to restrict its use. Potential near-term applications for devices such as chemical sensors (oxygen, pH), ceramic bearings, cam followers, and other smaller engine parts might be cost effective, assuming that ion implantation could solve problems. In the longer term, more economical ion implantation technology, coupled with minimal environmental impact, could make ion implantation attractive for wider use in basic economic areas such as utilities and transportation.

ACKNOWLEDGMENT

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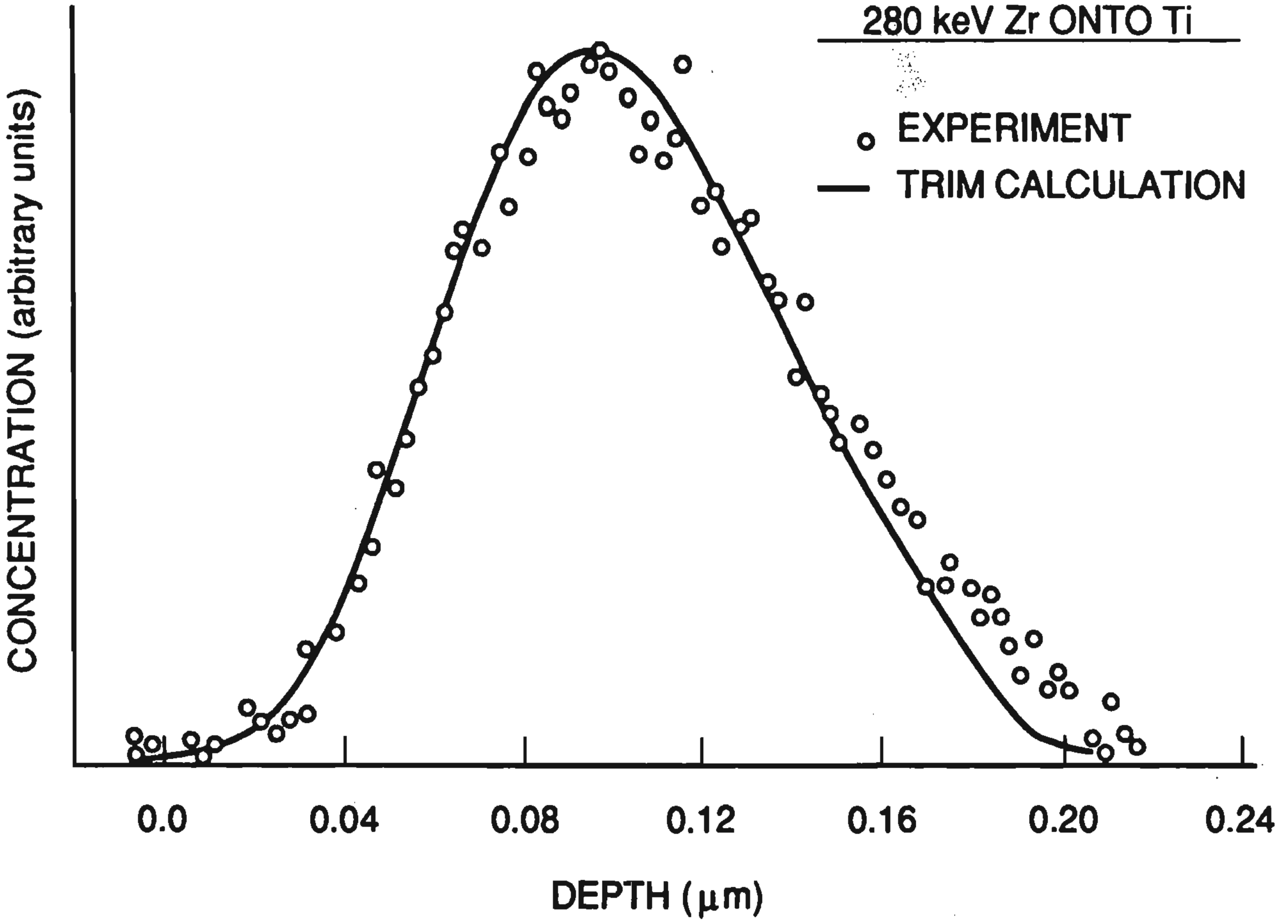

Figure 1. Concentration versus depth for 280 keV Zr ions implanted into a Ti-6 wt % Al-4 wt % V alloy. The experimental determination of the depth distribution by Rutherford backscattering spectrometry has been compared with that derived from a TRIM calculation.

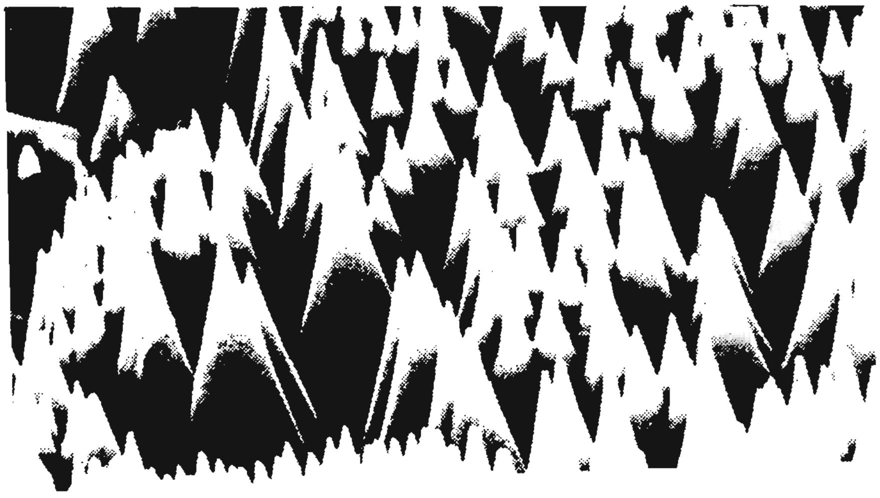

Figure 2. "Cones and pyramids" type of sputter texture produced on a copper surface by use of a huge dose ($1.5 \times 10^{19}/cm^2$) of Ar ions at 40 keV [3]. The breadth of the area is about 3 μm. Photograph courtesy of J. L. Whitton.

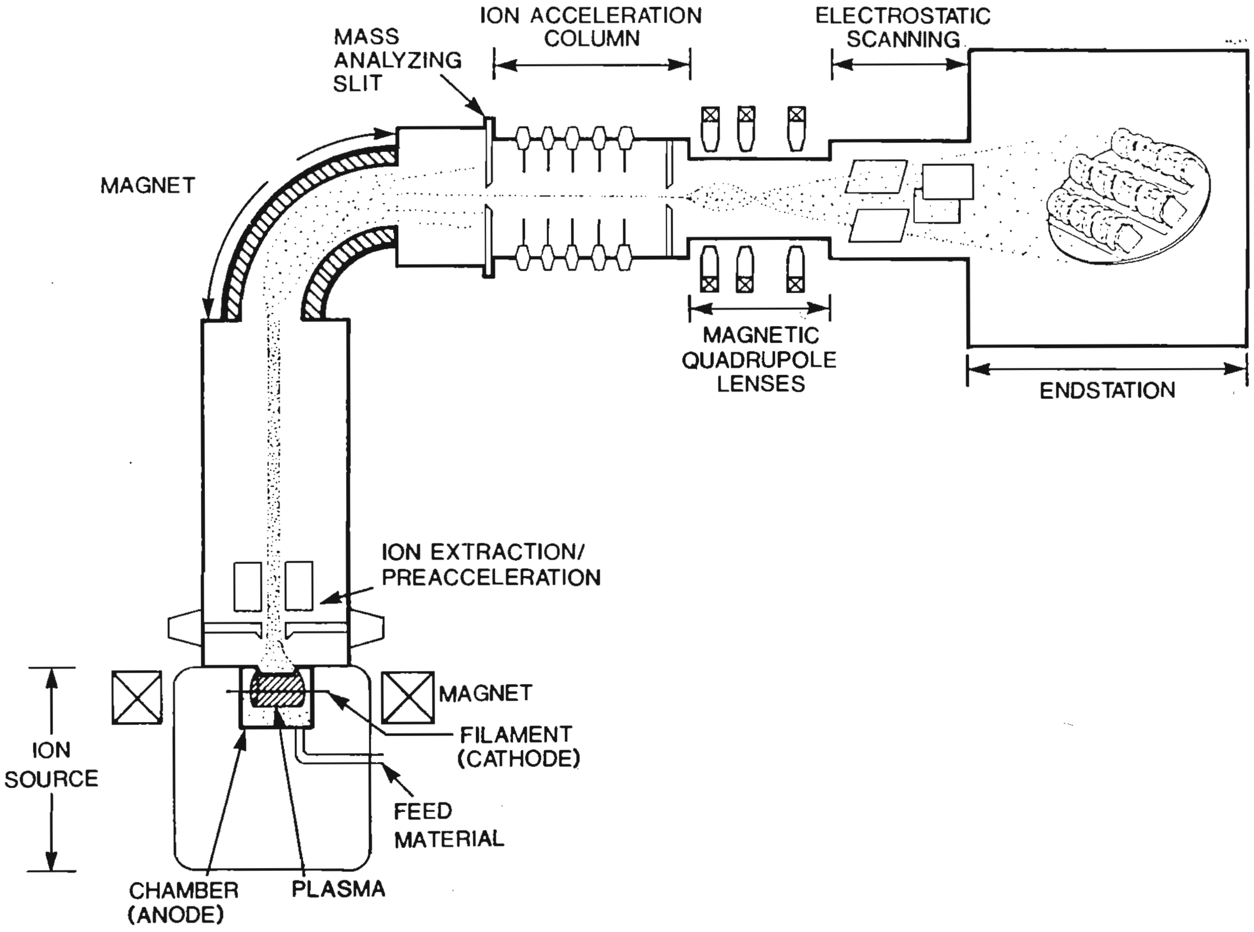

Figure 3. Schematic representation of a postacceleration type of ion implantation system, with magnetic mass separation of beam constituents. The target in the end station is intended to represent an array of orthopedic knee joints that are being treated for improvement of wear performance.

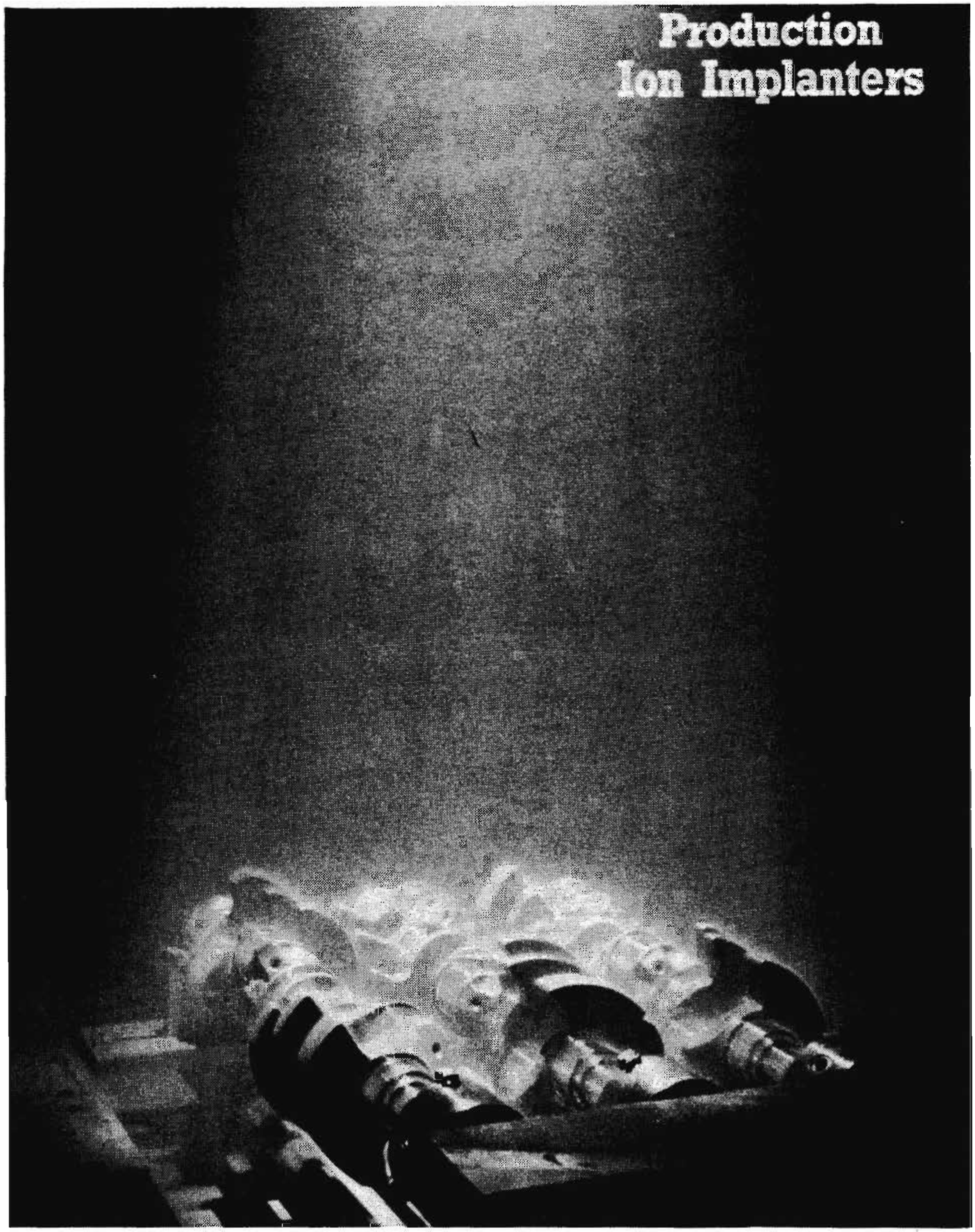

Figure 4. Automotive crankshafts undergoing N-ion implantation. The beam diverges as a cone from the source and is unanalyzed for mass, molecular, or charge content. This facility is at AEA Industrial Technology: Harwell Laboratory, United Kingdom. (Photograph courtesy of G. Dearnaley.)

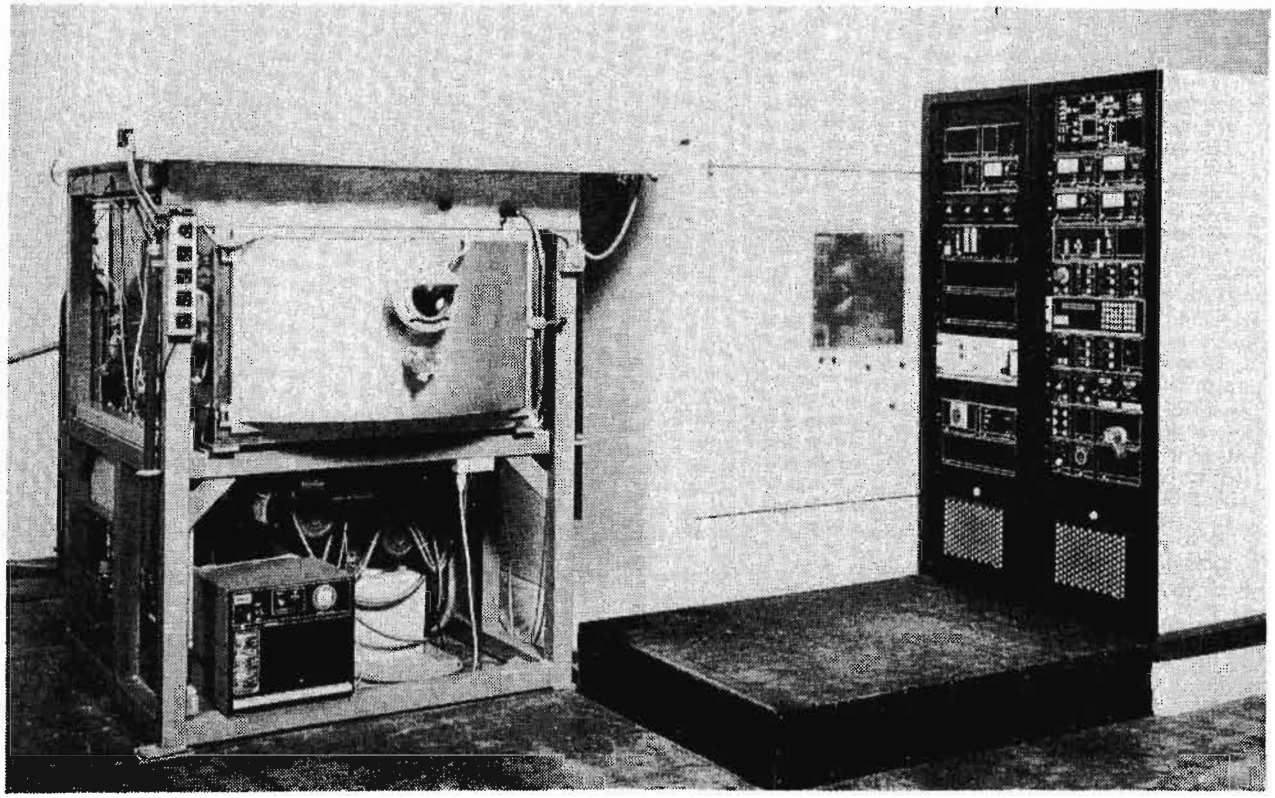

Figure 5. View of an ion implantation system intended primarily for use in ion implantation of large metallurgical products. This system is manufactured by Leybold and has capabilities similar to the system shown in Fig. 3.

INTEGRATED, HIGH CURRENT ION BEAM TECHNOLOGY
TARGET: BEAM PROFILE OF 50 cm x 5 mm

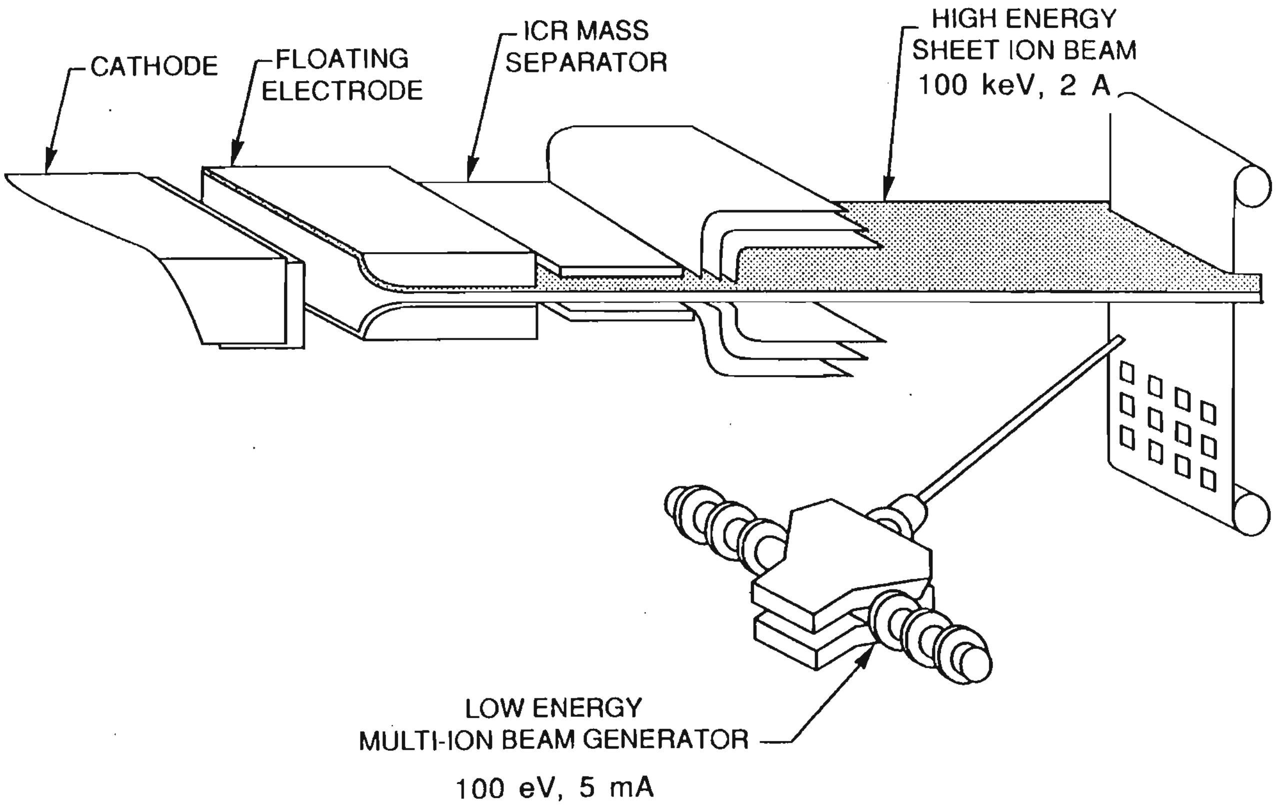

Figure 6. Schematic representation of the "sheet ion beam" type of ion implanter. Development of this device is being done by ULVAC Japan, Ltd. as part of the AMMTRA program.

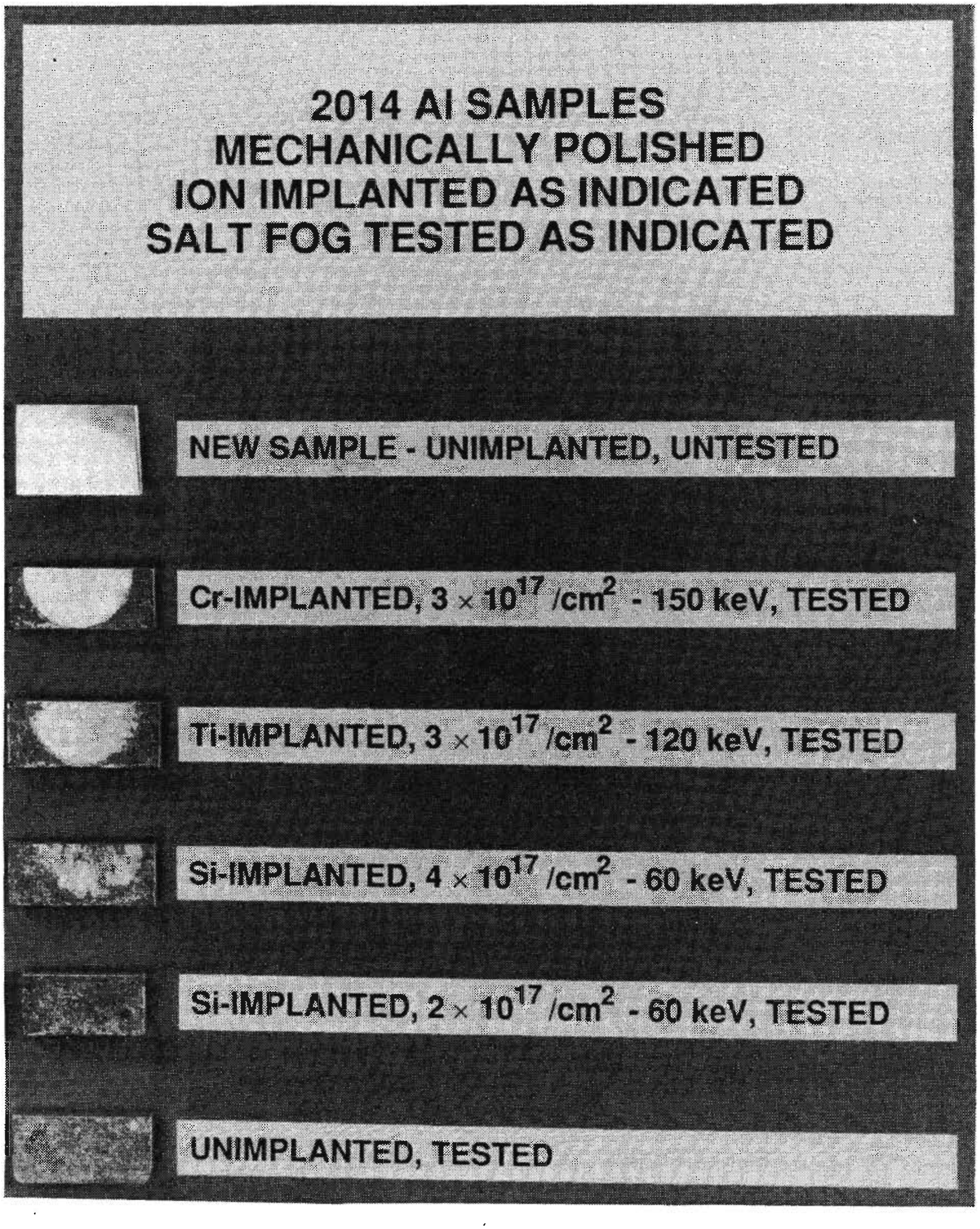

Figure 7. Photograph showing coupons of 2014 Al, new, after various ion implantation treatments and salt fog testing (168 h), and as-tested with no ion implantation. Initially, the surfaces were all mechanically polished. The ion implanted areas were 2 cm in diameter, and the implanted samples were halved after testing. Cr ion implantation was very effective, reducing corrosion to almost nil. Oxide patches on unimplanted areas were up 30 μm in thickness.

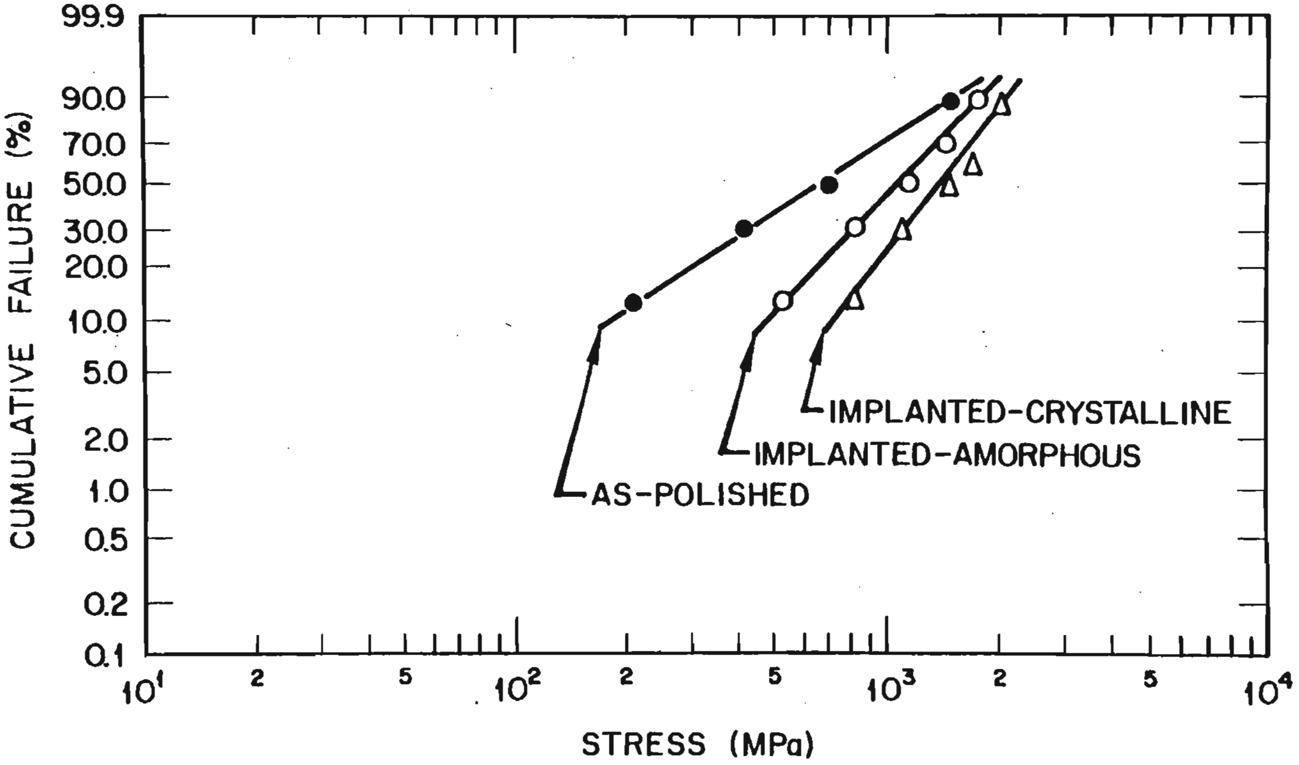

Fig. 8. Weibull analysis for fracture under four-point bending of an as-polished, implanted-amorphous, and implanted-crystalline Al_2O_3 specimen.

16. SURFACE TREATMENTS WITH ION BEAM ASSISTED DEPOSITION

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ABSTRACT

This contribution introduces ion beam assisted deposition (IBAD), reports on progress toward obtaining an understanding of the physical and chemical processes that are active during IBAD, and gives examples of applications that are currently in use or that are projected to be in use in the near future. Sufficient background is given that the reader should obtain a working knowledge of the technique, understand the advantages and limitations, and have a good idea as to how it may be applied to specific problems. In particular, a model is presented that includes the effects of sputtering, reflection of ions, multiple species beams, charge exchange neutralization, and incorporation of ambient gas atoms. Good agreement is found with data on several materials for the composition of films as a function of the arrival ratio of ions to evaporant atoms. Calculations based on a collision cascade simulation are reviewed that predict the energy dependence of the critical arrival ratio to achieve low intrinsic stress in deposited films. Factors that influence the choice of the geometry for beam assisted deposition systems, the choice of ion beam energy, and applications of the films are discussed in detail.

I. INTRODUCTION

Ion beam assisted deposition (IBAD) refers to the process in which evaporant atoms produced by physical vapor deposition (PVD) are simultaneously struck by a flux of low energy ions [1]. The extra energy imparted to the deposited atoms causes atomic displacements in the bulk and surface atom migration. This can result in improved film properties [2,3] that include better adhesion and cohesion of the film, modified residual stress, and higher density compared to similar films prepared by PVD [4,5]. When the ion beam or the evaporant is a reactive species, compounds such as refractory Si_3N_4 can be synthesized at very low temperatures [6].

There are many excellent review articles on IBAD films in the literature [1,7-11]. However, the majority of these papers focus on the film properties, and little attention is given to the physical aspects of film fabrication. In this article, the development of an understanding of the physical processes active during IBAD is presented, as well as film properties and applications [12]. Models are presented for the prediction of bulk physical properties of compound nitride films synthesized by IBAD. The models accurately predict the film composition and thickness for nonreactive species and the amount of ambient gas incorporated for reactive species. Applications are discussed in the areas of optical films, coatings for oxidation and corrosion protection, and tribological coatings.

II. BACKGROUND

It is interesting to trace the development of IBAD in the surface modification community. The pioneering work that demonstrated the superior properties of IBAD films was done chiefly by researchers in the field of optical thin films during the late 1970s and early 1980s. Surface modification by ion implantation at ~ 100 keV developed independently from the IBAD technique. However, it was always understood by the implantation community that the shallow depth of penetration was a major limitation to the development of certain applications. The advantages of PVD are the formation of thick films, a wider range of film composition, and low cost. The advantages of ion implantation are high adhesion, bulk density, low substrate temperature, good reproducibility and control, and absence of catastrophic stress levels. Note that the advantages of PVD are exactly the disadvantages of ion implantation and vice versa. The connecting line shows that IBAD combines the advantages of ion implantation and PVD and discards the disadvantages. Table 1 identifies the reasons why many researchers in the ion implantation community have expanded their interests to include the development of IBAD.

III. EXPERIMENTAL CONDITIONS

Figure 1 shows the most common geometry used in IBAD. Important details of the methods may be found elsewhere [12-14]. Briefly, a broad beam from an ion source (Kaufman gun) impinges on a substrate simultaneously with the deposited atoms. An electron beam source is the most common PVD source, but thermal sources, e.g., a Knudsen cell, or a sputter target in the case of dual ion beam sputtering, are also used. The most straightforward geometry for data interpretation and for the generation of uniform films is a small angle (< 30 degrees) between the vapor and ion sources. A 90-degree angle is also used when the beam is generated by an ion implanter. In systems that use a Kaufman ion source, the operating pressure is typically between 5×10^{-5} and 5×10^{-4} Torr, whereas in systems that use an external ion source (e.g., an ion implanter), the pressure can be much lower in the deposition chamber.

Ion beam energies between ~ 30 eV and 100 keV have been investigated. The appropriate energy is a matter of choice, often dictated by the equipment one has available to construct an IBAD system. Although there is no general agreement on the best energy to use for IBAD, some qualitative information

Table 1. Comparison of the advantages (+) and disadvantages (-) of ion implantation and physical vapor deposition (PVD) ion beam assisted deposition in which IBAD combines the advantages of both processes

Feature	Ion Implantation		PVD
	(-)		(+)
Thickness	100 nm		Micrometers
Concentration	< 40 at. %		0%-100%
Cost	High		Low
		IBAD	
	(+)		(-)
Adhesion	Excellent		Poor
Density	High (bulk)		Low (< bulk)
Stress	Low		High (delamination)
Substrate temperature	Low		High (for best film properties)
Reproducibility	Excellent		Fair
Control	Excellent		Fair

is available. Both M. Iwaki [15] and G. Wolf [14] report that while the adhesion of IBAD films is improved at low energies (500 eV to 3 keV), the best adhesion is obtained at higher energies (20 to 40 keV). On the other hand, Martin [9], Gibson [1], and others report that the absorption in optical films increases as the energy increases, due to a greater displacement damage, and they obtained their best results at energies below 500 eV. Therefore, a tentative conclusion is that the beam energy should be chosen according to the application of the film. For films intended for environmental protection, wear resistance, decorative coatings, etc., the high energy is suitable to obtain the best adhesion. Also, film damage is less likely to affect the important properties of corrosion resistance and hardness. For films intended for optical and microelectronic devices, low energy is preferred to minimize optical absorption and the formation of electrically active defects.

IV. PHYSICAL PROCESSES

Figure 2 presents the physical processes to be considered by a simple phenomenological model of the IBAD process that is discussed in greater detail by Van Vechten et al. [13]. Referring to Fig. 2, vapor atoms (indicated by V) impinge on the growth surface. The ions, which for the sake of discussion, consist of both N_2^+ and N^+, are either implanted beneath the surface or reflected with reflection coefficient r. As a result of ion bombardment, some of the deposited atoms are sputtered from the surface with sputtering coefficient S, and adsorbed ambient gas atoms (indicated by G) may be either desorbed or stimulated to chemically react with the surface atoms. Finally, in passage through the ambient gas, some of the ions are neutralized by charge exchange collisions, and therefore will not be counted by the charge collection system.

A. Model For Film Composition

Simple models have been proposed in previous work [12,13] to predict the composition of IBAD films in the synthesis of nitrides. A material system that particularly lends itself to quantitative study is silicon nitride, in which Si is evaporated and nitrogen ions impinge on the surface. Alloys of any composition $Si_{1-x}N_x$ up to stoichiometric Si_3N_4 are produced, depending on the value of the arrival ratio, R_a, of nitrogen atoms to silicon atoms.

The alloy composition, R_f, defined as the nitrogen to silicon ratio in the film is given by

$$R_f = R_a (1 - \langle r\rangle)/(1 - R_a\langle S\rangle) \tag{1a}$$

where

$$R_a = \langle\delta\rangle (1 + \beta) \gamma I_F/(e N_{Si} \gamma_c Q) \tag{1b}$$

In Eq. 1a, $\langle r\rangle$ is the effective reflection coefficient of nitrogen ions and atoms (0.10), and $\langle S\rangle$ is the effective sputtering coefficient of silicon (0.26). The parameter values were determined in previous work for a 500-eV nitrogen beam and an operating pressure of 2×10^{-4} Torr [13]. In Eq. 1b, $\langle\delta\rangle$ is the effective number of nitrogen atoms per unit charge (1.89), $1+\beta$ is the charge exchange correction factor (1.52), γ is the ion beam tooling factor (1.05), I_F is the ion current density (A/cm^2), e is the electron charge, N_{Si} is the atomic density of Si, γ_c is the tooling factor for the quartz crystal microbalance (1.05), and Q is the deposition rate of Si from the quartz crystal microbalance (cm/s). All of the parameters in Eq. 1b are independent of I_F and Q, so $R_a = K I_F/Q$, where K is a constant.

The film composition, R_f, is plotted in Fig. 3 versus I_F (bottom scale) and R_a (top scale) for films deposited in a pressure (N_2) of 2×10^{-4} Torr and at a deposition rate of 10 Å/s. The composition was measured by Rutherford backscattering spectrometry (RBS). The curve in Fig. 3 is calculated from

Eqs. 1a and 1b for the indicated parameters values. The agreement between the experimental points and the model is excellent. Assumptions included in the model are (1) there is no ambient gas incorporation, (2) N atoms not reflected are implanted beneath the surface, and (3) there is no diffusion or sputtering of N after coming to rest. These assumptions are applicable because (a) the curve extrapolates to $R_f = 0$ at 0 ion current, (b) one value of the sputtering coefficient reproduces the data at all currents (e.g., the surface binding energy is unchanged), and (c) all nitrogen is accounted for either by reflection or by incorporation into the film (e.g., there is no loss of nitrogen from the film).

Similar data for the boron nitride system [20] are plotted in Fig. 4. As was the case for Si, the data extrapolate to the origin indicating no gas incorporation into the film. The curve is a fit to Eq. 1a for the sputtering coefficient S where all the other parameters are fixed at the same values as for Si with the exception of r (r = 0 for BN). The fitted value of S is 0.11 ± 0.1 where the large error results from the limited amount of data obtained at high arrival ratios.

B. Model for Film Thickness

A model for the thickness of IBAD silicon nitride films was proposed in an earlier paper [16]. A useful quantity for the fabrication of compound films is the ratio of the thickness of the film deposited on the sample, D, to the thickness of silicon deposited on the quartz monitor, Q_t, which is called the thickness correction factor, T_c. It is expressed as

$$T_c = \gamma_e N_{Si}/N_a[R_a(1 - \langle r\rangle - \langle S\rangle) + 1] \tag{2a}$$

where the alloy atomic density is

$$N_a = \rho A/M = [2.28 + (\rho_{SN} - 2.28) R_f/1.33] A/(28 - 6R_f). \tag{2b}$$

In Eq. 2b, ρ is the density of the alloy, A is Avogadro's number, M is the atomic weight of the alloy, and ρ_{SN} is the density of amorphous Si_3N_4. Interpolation of density is linear in R_f. The Si density (2.28 g/cm^3) and amorphous Si_3N_4 density (3.13 g/cm^3) are used at the end points of $R_f = 0$ and 1.33, respectively.

Experimental data for T_c are plotted versus ion current density [13] in Fig. 5. The solid circles are D/Q_t where D was derived from fits to infrared reflection spectra. For the open circles, D values for a different set of samples were obtained by surface profile measurements. There is good agreement between the two methods. The solid curve is computed from Eqs. 1b and 2 with the parameters given earlier in this paper. For ion currents greater than about 100 μA/cm^2, the curve is in reasonable agreement with the thickness data, with deviations averaging less than 2%. For smaller ion currents, departures are much greater.

C. Incorporation of Ambient Gas Atoms

Materials that are amenable to the IBAD process are nitrides, oxides, and carbides. Frequently, a reaction will occur between the ambient gas (from the ion source or the backfilling of the chamber) and the evaporant (from relaxation of the first criterion for applicability of the model described previously). It is of basic interest to understand how the ion beam modifies and controls this reaction.

Figure 6 shows the composition R_f of titanium nitride films (closed circles) versus the arrival ratio N/Ti for a Ti deposition rate of 10 Å/s and a pressure of 2×10^{-5} Torr [17]. At zero ion current ($R_a = 0$), R_f of the film is about 0.4, which is in sharp contrast to similar data for silicon nitride (Fig. 3) where $R_f = 0$ at $R_a = 0$. At higher pressure (2×10^{-4} Torr), $R_f = 1.0$ at $R_a = 0$, and at lower pressures, the data collapses toward the solid curve that represents the calculated amount of nitrogen incorporated into the film from the ion beam. This must be true in the limit of very low pressures in which the amount of nitrogen ambient gas arriving on the surface is much less than the contribution from the ion beam. The triangles in Fig. 6 are obtained by subtraction of the curve from the data points and represent the amount of nitrogen incorporated from the ambient. To perform this subtraction, assumption (2) in Section IIIA is used, i.e., all of the nitrogen that is not reflected is incorporated into the films.

A useful way to analyze the data is shown in Fig. 7 where R^g_f, the amount of nitrogen incorporated from the ambient, is plotted versus the pressure/deposition rate ratio in (Torr/Å/s). Data for two different R_a values are shown. This method of data reduction has the advantage that the relative fluxes of ions, evaporation, and ambient gas are evident in the plot. At $R_a = 0$ (filled squares), the amount of gas incorporation changes from stoichiometric titanium nitride to pure titanium in a little over a two order-of-magnitude decrease in gas pressure or increase in deposition rate. This demonstrates the well-known phenomenon that high deposition rates produce higher purity films by reducing the impurity gas/evaporant impingement ratio. For $R_a = 0.25$, the curve is altered, and two interesting points may be noted. First, the data retain the same shape but shift to lower pressure/deposition rate values. This implies that one effect of the ion beam is to increase the sticking coefficient of ambient N_2 gas molecules to the surface. Secondly, the saturation value at a high pressure or low deposition rate decreases from 1.0 to about 0.86. This can be explained by a decrease in the active absorption sites on the surface as a result of ion bombardment or by desorption of adsorbed nitrogen.

A simple calculation was performed using a dynamic surface coverage model similar to one proposed by Barbie et al. [18]. The model is preliminary and is intended to demonstrate qualitatively which physical processes should be considered to explain the results. The model includes a surface coverage dependent sticking coefficient for physisorption and the concept of dynamic exposure time. The solid line in Fig. 7 is the calculated N/Ti ratio assuming a sticking coefficient of 0.1, a fraction of active surface absorption sites for N_2 of 0.5 monolayers, and a negligibly small thermal desorption rate. The curve is in reasonable agreement with the data for $R_a = 0$. The line corresponding to $R_a = 0.25$ (short dashes) is obtained by setting the sticking coefficient to 1.0 and reducing the surface active fraction of adsorption sites to 0.42. Thus, it is possible to infer two effects of bombardment: (1) the sticking coefficient for the N_2 increases by a factor of about ten, and (2) the number of active adsorption sites decreases approximately in proportion to R_a. A more complete model would account for the sputtering of surface adsorbed nitrogen, which could be part or all of the latter effect.

The expression used for the calculated curves in Fig. 7 has the form

$$q = \alpha(1 - \theta)E/(B - \theta/C)\ p/Q \tag{3}$$

where α is the sticking coefficient of nitrogen on a pure Ti surface, θ is the fraction of the adsorption sites filled, p is the pressure, E is a constant, and the constants B and C include the desorption rate (assumed to be very small), surface migration rate (assumed to be very small), and rate of conversion from physisorbed to chemisorbed states (~ 0.1). The agreement of the model with the data is encouraging. It may be anticipated that with further development, it will be possible to derive an expression for composition that will have the form

$$R_f = R_f^b\,(R_a) + R_f^g\,(R_a)$$

where the first term is Eq. 1, and the second term is derived from Eq. 3.

V. FILM PROPERTIES

Some of the enhanced properties of IBAD coatings are listed in Table 2. The following section gives examples that illustrate the differences between PVD films and IBAD films.

A. Adhesion and Stress

Figure 8 shows a photograph of a 2-μm-thick film of Si deposited on Ta. The delaminated film (hairy Si) on the left side of the photo was shielded from a 1000-eV nitrogen ion beam, while the right side was bombarded at an arrival ratio of 0.2. The film is uniform and very adherent and does not delaminate due to high internal stresses. This is one of the primary advantages of IBAD films—high adhesion and reduced internal stresses.

Figure 9 shows the stress in W films [19] as a function of substrate temperature and arrival ratio of Ar ions. Note that at each temperature, there exists an arrival ratio at which the stress is zero, and that with no ion beam, the film contains high levels of residual internal stress. These data are quite typical for IBAD films, e.g., stress can be reduced in most materials. High stress leads to rupture and delamination above a critical thickness, and it is common for PVD films of dielectrics, semiconductors, and refractory metals to have high stress. Therefore, IBAD offers a means to control the stress that facilitates the production of very thick films.

B. Densification: Theory and Experiment

The most important practical attribute of IBAD is the increase in film density over PVD films. PVD films typically contain voids or columnar structures that produce a 10% to 20% density deficit relative to the bulk material [20,21]. This is especially true for covalently bonded semiconductors and refractory metals. The densification mechanism is poorly understood. It is well established that the energetic ion beam applied to the film in the IBAD process can eliminate the voids and produce bulk density films. The mechanism for this densification may be related to atomic displacements in the collision cascades, enhanced surface and bulk diffusion, recoil implantation, and ion mixing mechanisms. A particularly revealing experiment has been performed by Hirsch and Varga regarding this issue [22]. Germanium was deposited with Ar ion assistance for Ar ion energies between 65 eV and 3000 eV. Hirsch and Varga found an energy dependent critical arrival ratio of ions to atoms, R_c, above which the 2-μm-thick films on Ge substrates did not spontaneously delaminate from the surface. Hirsch and Varga suggested that if sufficient energy is provided to the growing film, internal stresses in the film are reduced

Table 2. Classification of the three modes of film formation for ion beam assisted deposition

Ion Assistance			Ion Assistance (Compound Synthesis)			Reactive Ion Assistance (Gas Adsorption)		
Vapor	Ion*	Film	Vapor	Ion*	Film	Vapor	Ion*	Film
Ge	Ar	Ge	Si	N	Si_3N_4	Ti	N	TiN
Ag	Ar	Ag	B	N	BN	Ti	Ar	TiN
CeO_2	O	CeO_2	Si	CH_4	SiC	Nb	N	NbN
Ta_2O_3	O	Ta_2O_5	Cu	O	Cu_2O	Al	O	Al_2O_3

*The ions consist of both atomic and molecular ions and may be more than singly charged.

to a level that allows the growth of thick Ge films. The crosses in Fig. 10 show the data that Hirsch and Varga fit with the functional form $R_c \alpha\ E^{-3/2}$.

Brighton and Hubler analyzed these data by means of the binary encounter approximation (BEA) for the simulation of collision cascades [23]. They pointed out that the energy dependence of R_c could be reproduced by assuming that the reduction in stress is directly related to the total energy lost to displacement collisions. For reduced energy units of $\varepsilon < 0.1$, the energy dependence of the nuclear energy loss, dE/dx varies as $E^{1/2}$. If the reduced stress is caused by the total amount of energy expended in displacement collisions, then the total energy is obtained by integrating over the ion energy, or

$$R_c = \int_E^o \frac{1}{dE/dx}\, dE = E^{-3/2}\ ,$$

which was observed by Hirsch and Varga. If the reduction of stress were caused by enhanced surface atom mobility from energy deposited at the surface, then the energy dependence

$$R_c\, \alpha\ \frac{1}{dE/dx} = E^{-1/2}$$

would be expected. Thus, it is possible to distinguish between surface and bulk mechanisms by measuring the energy dependence of R_c for a particular property of the film.

Brighton and Hubler also calibrated the BEA Monte-Carlo code MARLOWE [24] by adjusting the input parameters to reproduce ion range and sputtering yield data for the Ar ⇒ Ge system at low energies. Assuming that every deposited atom had to be involved at least once in a collision cascade at the critical arrival ratio (similar to a radiation damage level of one displacement per atom), Brighton and Hubler calculated the points in Fig. 10 represented by circles. This calculation contains no adjustable parameters, and the absolute agreement with the data is quite good. This result supports the assumption that reduction in stress occurs when every deposited atom is involved in a cascade.

The physical reason for reduction in stress was assumed to be caused by densification of the film where the voids were eliminated by the collision cascade, but no analysis of the films was carried out by Hirsch and Varga to confirm this. Recently, Yehoda et al. [21] have measured by means of transmission electron microscopy (TEM) the arrival ratio of Ar ions to Ge atoms, which eliminated voids in PVD Ge films. They found a 9% void density without bombardment and full bulk density with bombardment at arrival ratios that match well with those of Hirsch and Varga. These experiments are convincing evidence that the densification of Ge films grown with the IBAD process occurs during the collision cascade and that the reduced stress is a result of that densification. This conclusion is also in accord with two-dimensional molecular dynamic simulations carried out by K. H. Muller [25] that give a detailed picture of the cascade events that produce densification.

It is interesting to note that the data of Hirsch and Varga and the analysis of the data can be used to optimize the IBAD process. One can choose an arrival ratio to increase film density, yet minimize the amount of incorporated Ar, which usually increases with increasing R.

An experiment on the Ar ⇒ Cr system at higher energies (3-20 keV) by G. Wolf and his students [14] indicates that the energy dependence of the critical arrival ratio to achieve zero stress in films is E^{-1}. This important work is only the second comprehensive study of its type (after Hirsch and Varga) and it provides an important clue about the stress relief mechanism. Two important differences with the Hirsch and Varga study are (1) higher energy and (2) a metallically bonded system as opposed to a covalently bonded system. Both differences may be responsible for the different energy dependence. More theoretical work is required to explain these results.

The above discussion shows microscopic evidence for densification induced by ion bombardment. Figure 11 presents film density of ZrO_2 films bombarded with 1200 eV O_2 ions. This is a direct measurement of the change in density of the film [26].

C. Microstructure

The effects of ion beams on the microstructure of films are numerous and complicated. For this reason, only some general observations will be noted here, to give a flavor of the modifications that are observed.

Most covalently bonded materials such as semiconductors and silicon nitride or silicon carbide ceramics will be amorphous at room temperature. Silicon and germanium will be crystalline above the temperature of ~ 0.4 T_m, the melting temperature in degrees Kelvin. Using ion beam deposition, the temperature may be lowered by ~ 200 K because the atomic motion induced by the energetic atoms serves the same purpose as high substrate temperature [7]. Metals and ionic materials tend to be polycrystalline.

In general, the ion beam decreases the grain size at low temperatures, but can increase grain size at higher temperatures in which annealing effects overcome the damage caused by the ion beam [7]. This small grain size is partly responsible for the general observation that IBAD films are more ductile than bulk materials with a larger grain size.

The orientation of films can be altered so that textured films are commonplace. The degree of texturing is dependent on beam energy, beam flux, and substrate temperature. In some cases, epitaxial films can be induced to grow with ion assistance where they do not grow in the absence of ions. Ni and Al on silicon are examples of this [7].

VI. APPLICATIONS

Applications are quite numerous in the optical thin-film industry, where the primary advantage offered by IBAD is film densification. Refractive index stability and freedom from environmental degradation are direct benefits of IBAD. Research in the area of wear-resistant and corrosion-resistant coatings for metals and ceramics is just beginning. In general, there are three classes of IBAD, which are summarized in Table 2. In each column are several examples of the material system deposited for one of the three classes.

The first column shows a simple ion assistance type in which inert heavy ions such as Ar are used to improve the properties of an elemental film or a compound film that undergoes congruent evaporation. In this case, it is important to minimize the amount of Ar incorporated into the film; that amount increases with R_a and beam energy. Therefore, the lowest R_a possible to obtain the desired film properties should be used. An improved understanding of the critical arrival ratio to achieve improved films would be helpful in this regard. This class also includes materials such as CeO_2, which is slightly substoichiometric when evaporated by PVD. Ion assistance with Ar can be used for densification only, or oxygen ions can be used for densification and to restore stoichiometry.

The second column shows an ion assistance and compound synthesis group in which there is little reaction probability of the ambient gas with the evaporant. The third class in column 3 covers compound synthesis of very reactive materials. It can operate with the gas associated with the ion beam (e.g., N_2 for TiN), or inert ions such as Ar can be used in conjunction with a secondary gas supply of N_2 in which the purpose of the ions is to activate and control surface chemical reactions.

The models reviewed here potentially apply to all of these classes of IBAD. The first industrial application of IBAD for wear or corrosion resistance appears to be the coating of electric razor screens with TiN [15]. In this case, the choice of IBAD was dictated by the superior adhesion of the films over other methods. Table 3 is a comprehensive compilation of materials that have been grown with IBAD taken from the review by Smidt [7]; it has all the materials in the literature through 1989.

In order to place IBAD in the proper context with respect to potential applications, the following sections give examples of where IBAD is being used or where it is projected to be used in the near future. In this way the reader will have a grasp of the kind of materials and problems in which IBAD can potentially be employed.

Table 3. Partial list of materials deposited by ion beam assisted deposition

SiO_2	Si	Si_3N_4
Al_2O_3	Ge	AlN
TiO_2	a-Si:H	AlON
ZrO_2	InSbBi	SiON
CeO_2	GaAsGe	TiN
Ta_2O_5	GaSbSn	TiC
Cr_2O_3	GeSn	ZrN
VO_2		HfN
HfO_2		BN
InSnO		MoN
CuO		NbNC
MgF_2		MoS_2
ZnS		Diamond-like C
ZnSe		WSi_2
PbS		$YBa_2Cu_3O_{d-8}$
LaF_3		
ThF_4		

A. Optical Films

1. Densification of Optical Films

As already stated, the IBAD technique was initially advanced by workers interested in optical thin films. There are two kinds of applications: (1) those in which densification is the primary concern and (2) those in which graded refractive index profiles are required.

For the first kind of application, densification, low energy Ar or O ions are used to bombard the optical thin films. Research has shown that the density is increased, in some cases up to that of bulk material. The primary attraction is not necessarily that the refractive index is increased to near bulk values, but that the index value is stable under humidity and temperature variations because there are no voids or pores in the film that adsorb water vapor. This simplifies optical coating design and promotes better control and reproducibility in the fabrication process. Another benefit of using low energy ions is that adhesion to the substrate is improved, which also helps to increase production yields.

Figure 12 shows how the stability of ZrO_2 films is improved using IBAD. The IBAD film is completely immune from spectral shifts [26].

2. Graded Index Coatings

IBAD is beginning to be used to fabricate graded index coatings for antireflection coatings, reflection filters, and mirrors. Some of these devices can be tens of microns thick, so stress control becomes very important.

Figure 13 shows the data of Donovan et al. [27], in which the refractive index of silicon nitride films is plotted versus the nitrogen fraction x. The index varies smoothly between 3.9 and 2.0. This large and continuous change in index can be used to fabricate a new type of optical filter called a "Rugate filter," in which the refractive index profile varies sinusoidally in depth. This profile simulates a quarter wave stack interference rejection filter, and similar mathematical formalism may be used to predict the peak reflection frequency. The advantages of the Rugate filter versus the quarter wave stack are that (1) no interfaces initiate delamination and scatter light and (2) side bands away from the design frequency are minimized.

Figure 14a shows the deposition record for a Rugate film in which the N ion current/Si deposition rate ratio is plotted against the thickness. An increase of the ratio implies a reduction in the index. The Si deposition rate is held constant while the ion current is varied to produce the modulated composition. A computer controls the process by comparing the present ratio with a preprogrammed composition profile. This produces a modulated refractive index profile according to the data in Fig. 13. The solid curve in Fig. 14b is the optical density of the same film versus wavelength, and the dashed curve is a calculation directly from the deposition record. Agreement is very good above the absorption edge of the silicon substrate, which is not included in the calculation. Reflectance at the design wavelength of 1.1 µm is 99.5%. This is the first report of continuous modulation of composition by means of the IBAD technique.

Graded index antireflection coatings and broad band mirrors can be deposited in a similar fashion.

3. Optical Absorption

Figure 15 shows the change in absorption coefficient in the visible as a function of the energy of the Ar ion beam during deposition of Ta_2O_5 films [28]. As stated previously, lower energy beams reduce the displacement damage in the films that can produce color centers. Therefore, in general, low energies are desired for the deposition of optical films that operate in the visible.

It is difficult to assess how widespread the use of ion beams is in the optical film industry because the manufacturers have a need to protect proprietary methods.

B. Ion Beam Deposition

Several groups are depositing diamond-like carbon (DLC) by direct ion beam deposition. Using a Kaufmann ion source, methane is introduce into the plasma, and, at energies between 100 and 1000 eV, DLC is deposited with rates from 1-10 Å/s. DLC provides a hard, protective coating for optics and windscreens on vehicles. While DLC absorbs strongly in the visible, coatings from 200 to 2000 Å in thickness remain transparent enough to be used as protective transmission coatings. At least two companies are set up to produce these coatings over reasonably large areas (20-cm diameter). Advantages of these coatings are low porosity, high scratch hardness, and high adhesion to any substrate.

C. Corrosion

Because IBAD films are dense and have few pin-holes, they are attractive for corrosion protection applications. Although only a few studies on corrosion have been done, the early results look promising. Wolf has done IBAD Pt, TiC, TiN, B, DLC, CrN, BN, Cr_2O_3, and Si on metals with good success [14], and others have done Al, Ta, and W on carbon steel. Carbon steel is cheap and workable, and IBAD films have good adhesion and high corrosion resistance. Thus, even though the process may be expensive, use of inexpensive substrate material can obviate some of the processing cost.

Ceramic compound films such as Al_2O_3, Si_3N_4, and TiN also offer excellent corrosion resistance. Takahashi in Japan [29] has set up a processing line that coats steel sheet continuously with Al, TiN, or Al_2O_3. Figure 16 is a schematic of the apparatus. IBAD films are desirable, in part, because they are adherent and more ductile than bulk materials due to their microcrystalline or amorphous structures. Therefore, they can yield with the metal sheet so that some working of the metal is possible after application of the coating. Figure 17 shows potentiostatic polarization data for Si_3N_4 IBAD coatings on Al in a pitting solution [30]. The pitting potential of the coating is increased by 1000 mV, a very impressive increase.

D. Oxidation

Work on oxidation protection is recent with only one result in the literature using IBAD coatings of BN, Cr, or Si_3N_4 to protect Ti alloys. This seems to be a promising area for further research.

E. Catalysis

Ceyer has produced exciting increases in catalytic yields by bombarding a gas-catalyst surface with energetic neutral atoms [31]. This is an interesting result that may result in the fundamental understanding of gas-phase catalysis and perhaps in the design of new catalytic reactors.

F. Ion Induced Chemical Vapor Deposition

Several researchers have used class 3 of Table 3 for the production of unique hydrocarbon or ceramic films. In this process, a gas is introduced into the chamber, the substrate is cooled to induce condensation of the gas, and an ion beam strikes the surface. In this process, hydrocarbon bonds are broken, volatile species are released, and a coating is produced. For silicone oil vapor, and depending on the arrival ratio of ions to vapor-condensed atoms, the films can be very low friction solid lubricants to very hard, corrosion-resistant SiO_xC_y coatings [32]. This process is similar to chemical vapor deposition (CVD), in which the high temperature of the substrate provides the energy to initiate chemical reactions that are responsible for film formation. In the ion beam case, the same or similar reactions can be induced at room temperature, opening the possibility of depositing CVD-like films on polymers and other temperature-sensitive substrates.

G. Friction and Wear

IBAD is being used to deposit solid lubricant coatings such as MoS_2. Advantages are that the coatings adhere to the substrate and have a longer lifetime as a result of densification (better coherence).

The hardness of TiN coatings can be varied over a large range by microstructure control. Figure 18 shows the hardness as a function of arrival ratio for these films [33]. It is also true that the ductility of these films, even for the highest hardness, is much larger than that for bulk material or CVD TiN films. Boron Nitride, ZrN, and Si_3N_4 films have been investigated for wear properties. BN works extremely well on Si, but does not work particularly well on metals, and Si_3N_4 has good load bearing capability, but has a high friction coefficient, and is not well suited to sliding wear situations without the additional low friction coating over it. Many more materials need to be investigated. At the moment, the MoS_2, TiN, and silicon CVD are fairly well developed and work very well.

H. Low Energy Ion Beam Sputtering

NASA has performed unique research on developing high emissivity thermal control coatings using ion beam sputtering [34]. By arranging a target near the surface to be treated that seeds the substrate with an impurity, NASA researchers produce surfaces with a topography consisting of steep angle cones that absorb light. These surfaces have very high emissivity. Figure 19 shows the features of one of their surfaces. These materials hold great promise for long-life thermal control, and light baffle applications on satellites.

VII. SCALE-UP

Many of the applications described above require large areas to be coated. Ion guns of more than 60 cm in length are currently available, and at least one laboratory has a system that can handle 1-m-diameter workpieces. In nonoptical applications, in which uniformity of the film is not a strict requirement, very large areas could be done with present equipment by routine manipulation of the workpieces. To date, a diameter of about 20 cm is the record for uniform optical films.

Still higher surface areas are possible by the means of continuous coating schemes like that shown in Fig. 16. The primarily obstacle for scale-up is the requirement of line-of-sight processing, especially for odd-shaped parts. Cylinders can easily be coated, but it is not yet clear whether or not shapes like gear teeth can be reliably coated.

VIII. SUMMARY

As a surface modification technique, IBAD retains the best features of PVD and ion implantation and eliminates the worst features. The choice of the appropriate beam energy is determined by a trade-off between attaining the best film adhesion and minimizing the defects in the films produced by displacement damage. More measurements of the energy dependence of critical arrival ratios to achieve densification, improved adhesion, or low stress are needed to elucidate the mechanisms that improve film properties.

Simple models for the composition and thickness of silicon nitride and boron nitride films are in good agreement with experimental data. For the reactive titanium nitride system, a preliminary model for the amount of N_2 gas incorporated into the film was presented. The good agreement with the data is encouraging, but more development is necessary. These early results raise the expectation that a phenomenological model can be derived that will predict the composition of IBAD films in the general case of any ion/evaporant combination.

The application of IBAD films as wear- and corrosion-resistant coatings for metals and ceramics is just beginning. Because thick (~ microns) films are readily produced, IBAD will be more easily accepted and more widely used in industrial applications than will ion implantation.

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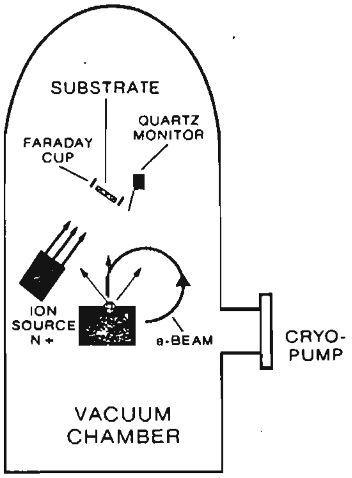


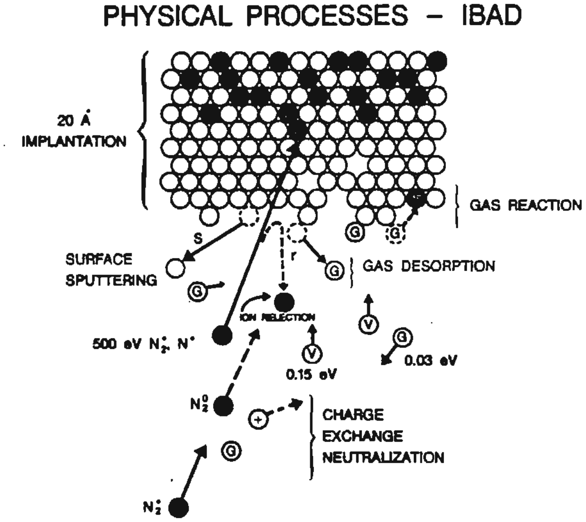
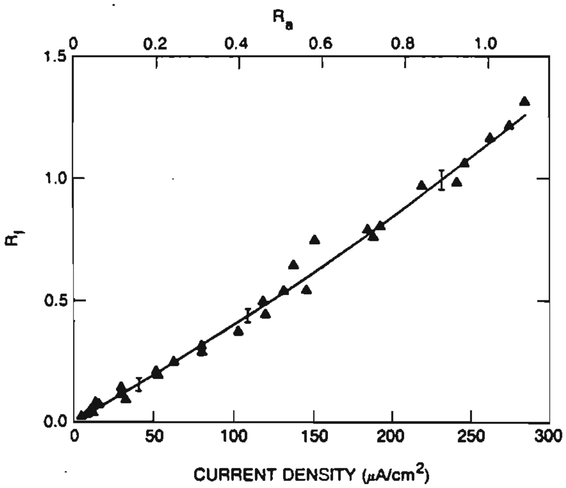


Figure 1. Schematic diagram of a typical ion beam assisted deposition (IBAD) system.

Figure 2. Schematic representation of the physical processes occurring during IBAD.



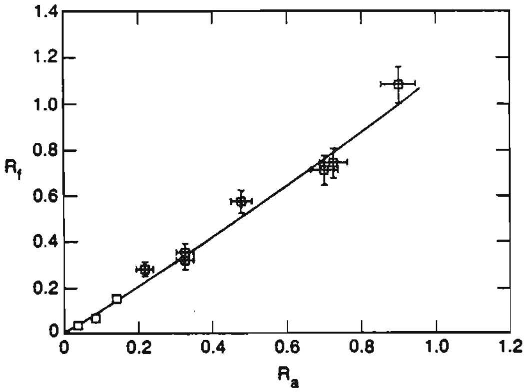
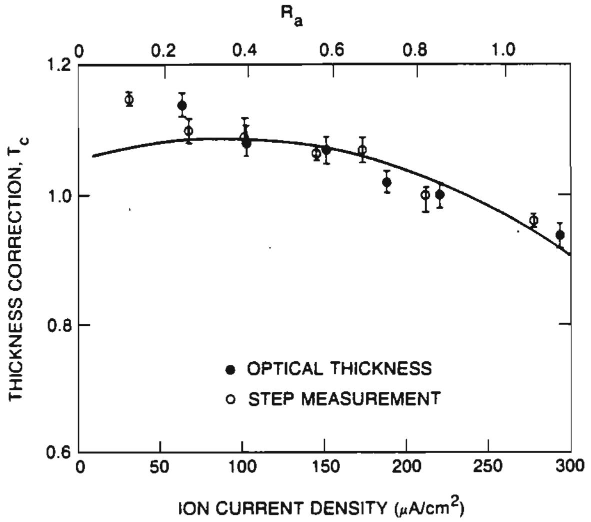


Figure 3. Composition ratio (N/Si) of IBAD films vs. the current density of 500-eV nitrogen ions (bottom) and the arrival ratio (N/Si) (top). The deposition rate of Si was 10 Å/s. Typical error bars are shown at three different current values. The curve is calculated from Eq. 1.

Figure 4. Composition ratio (N/B) of IBAD films vs. the arrival ratio of N/B. The deposition rate of B was 3 Å/s. The curve is calculated from Eq. 1a.



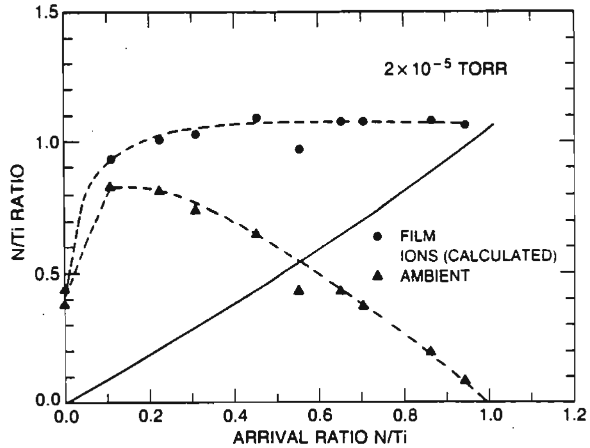
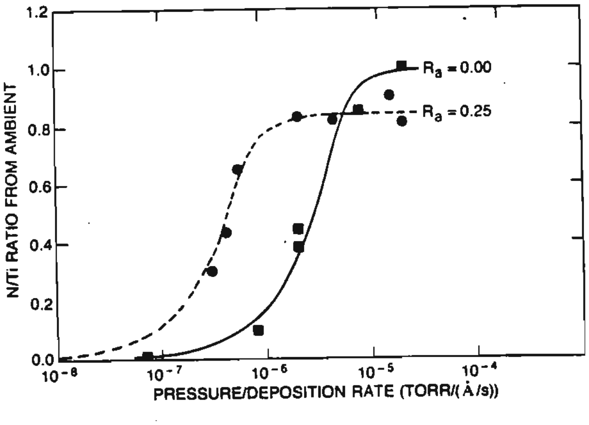


Figure 5. The thickness correction of IBAD films vs. current density of 500-eV nitrogen ions. The Si deposition rate was 10 Å/s. The open circles are from step height measurements, and solid circles are optical thickness measurements. The solid curve is calculated.

Figure 6. The composition ratio (N/Ti) of IBAD films vs. the arrival ratio N/Ti for 500-eV nitrogen ions and a Ti deposition rate of 10 Å/s (solid circles); N/Ti from implantation of nitrogen ions (solid curve); N/Ti from N_2 gas incorporation (triangles). The pressure of N_2 was 2×10^{-5} Torr.



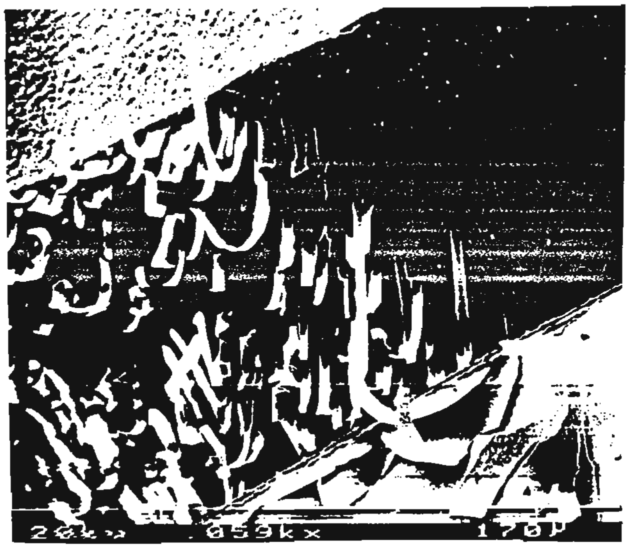


Figure 7. Contribution to composition ratio (N/Ti) from N_2 gas incorporated in IBAD TiN films vs. pressure/deposition rate ratio. R_a = 0 (squares), R_a = 0.25 (circles). Curves are calculated from Eq. 3.

Figure 8. Microphotograph of a 2-µm-thick film of Si deposited onto Ta showing delamination (left side). The left side was shielded during bombardment; the right side was bombarded during deposition with a 1-keV nitrogen ion beam with an arrival ratio of 0.2.

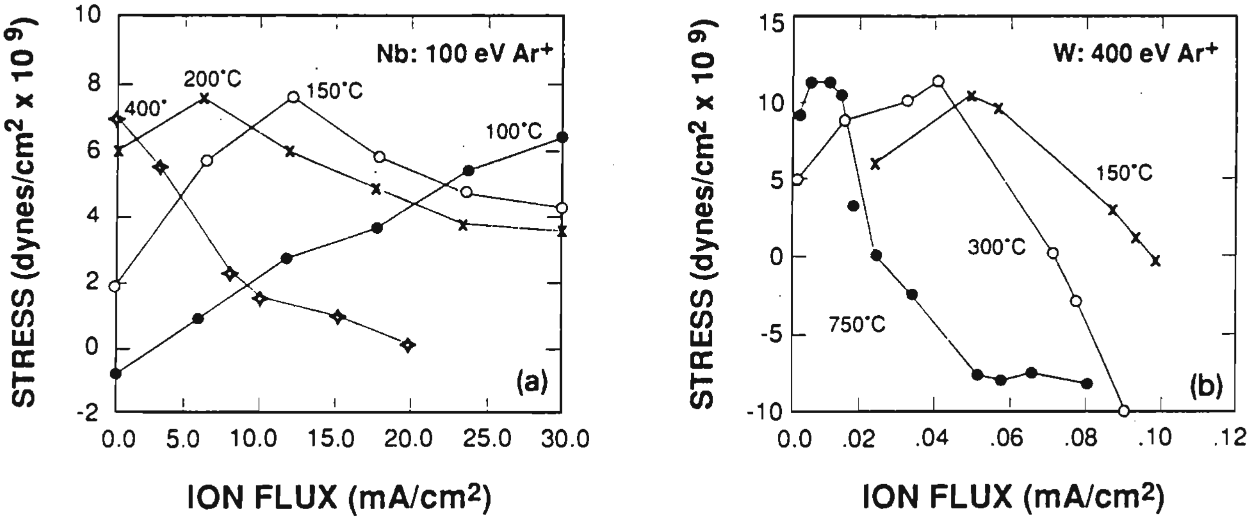
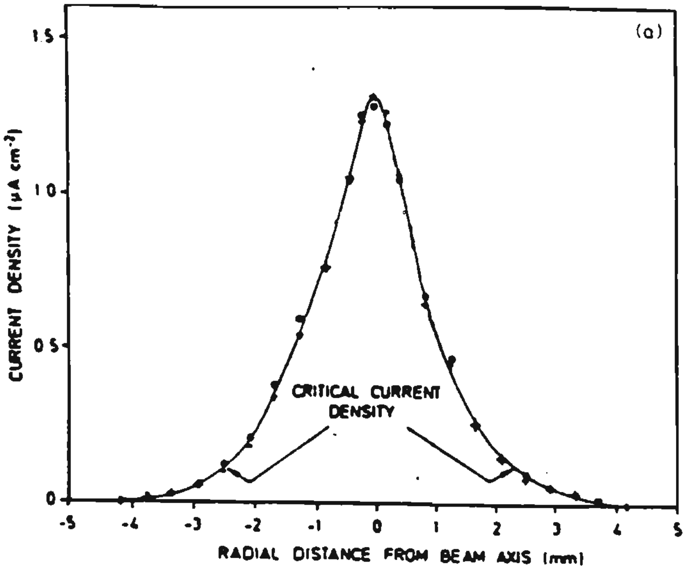


Figure 9. Stress as a function of ion flux (a) in Nb films evaporated with concurrent 100-eV argon ion bombardment and (b) for evaporated W films subjected to 400-eV concurrent ion bombardment shown at a series of substrate temperatures. A tensile stress maximum shifts toward lower ion flux as the substrate temperature is raised.



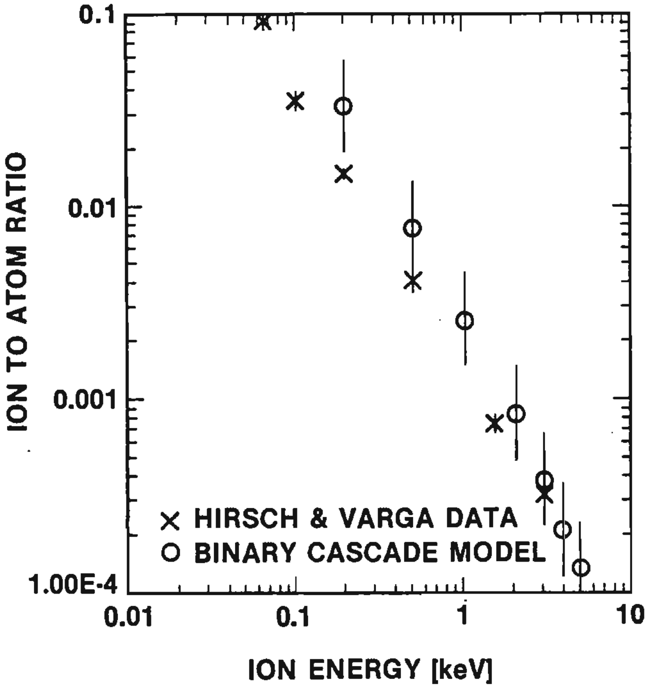
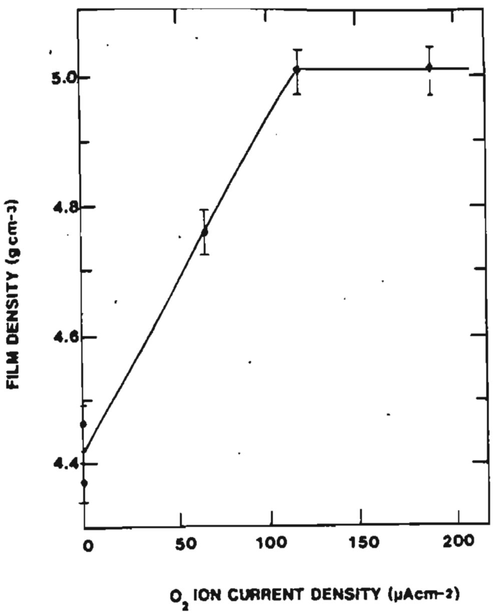
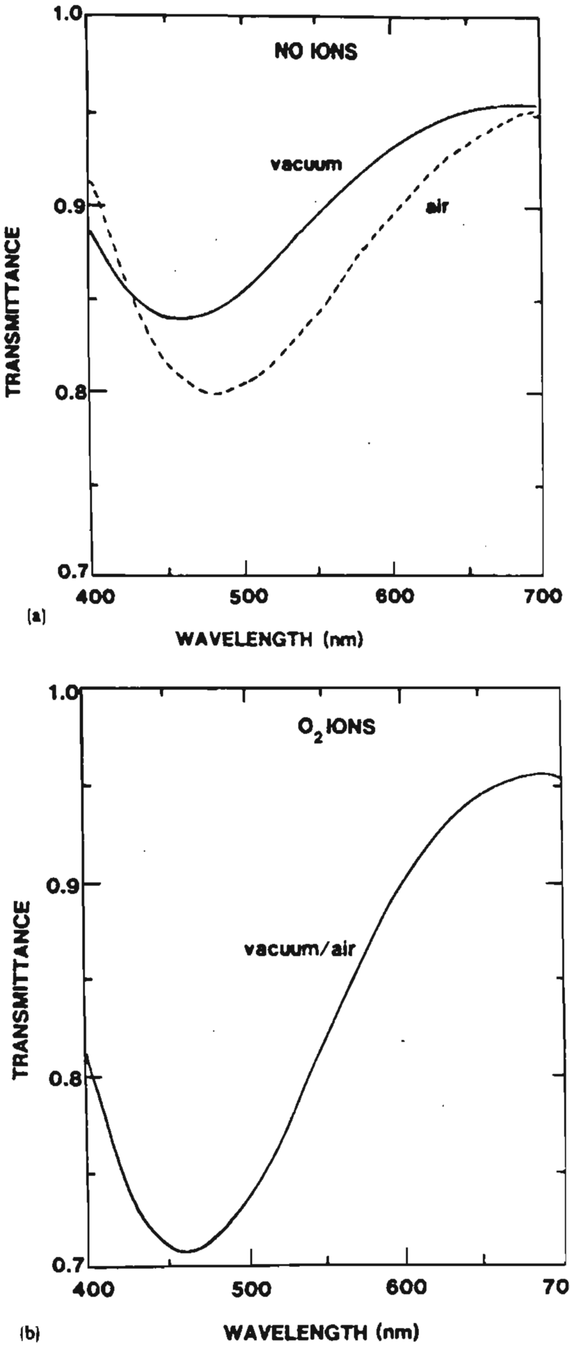


Figure 10a. A beam profile used to determine the critical current density for obtaining adhesion in Ge films [22].

Figure 10b. Critical values of the ion/atom arrival ratio for obtaining adhesion for various energy ion beams [2].





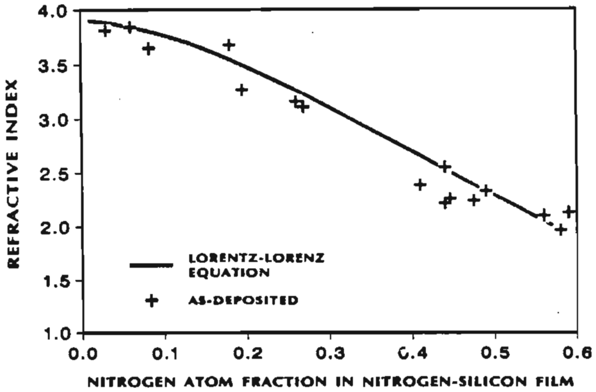


Figure 11. Change in film density with current density for ZrO_2 films prepared by IBAD with 1200-eV O_2^+ bombardment.

Figure 12. Transmittance of ZrO_2 films prepared (a) by evaporation and (b) with bombardment by 1200 eV O_2^+ ions. The change in transmittance when film is removed from the vacuum system can be eliminated by use of IBAD.

Figure 13. Comparison of the variation in the refractive index with nitrogen atom fraction in SiN_x for experimental results (circles) and calculations with the Lorentz-Lorentz equation.

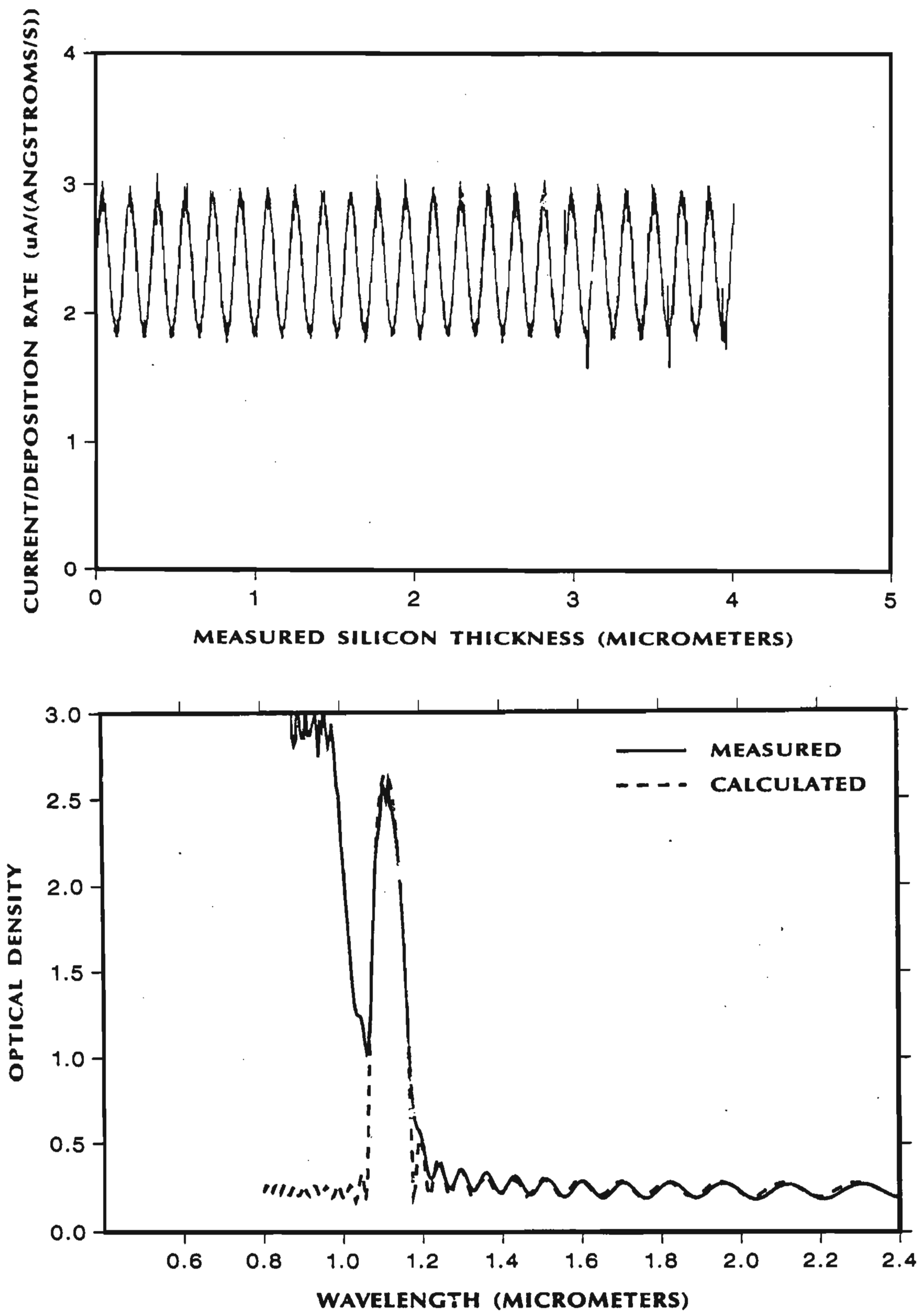


Figure 14. (a) Deposition record of a 23-cycle Rugate filter prepared on a silicon substrate. (b) Optical density vs. wavelength for the Rugate filter of (a) after a 750°C anneal.

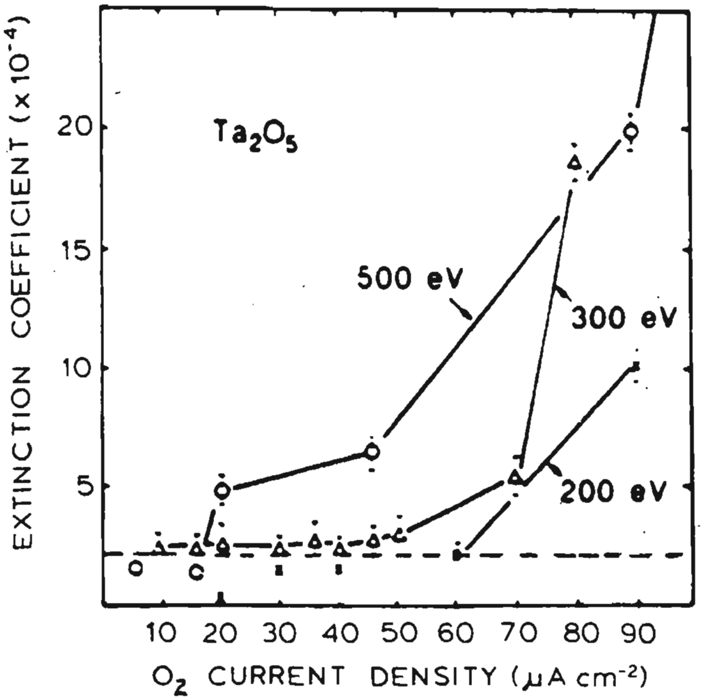


Figure 15. Changes in extinction coefficient for Ta_2O_5 films prepared by IBAD.

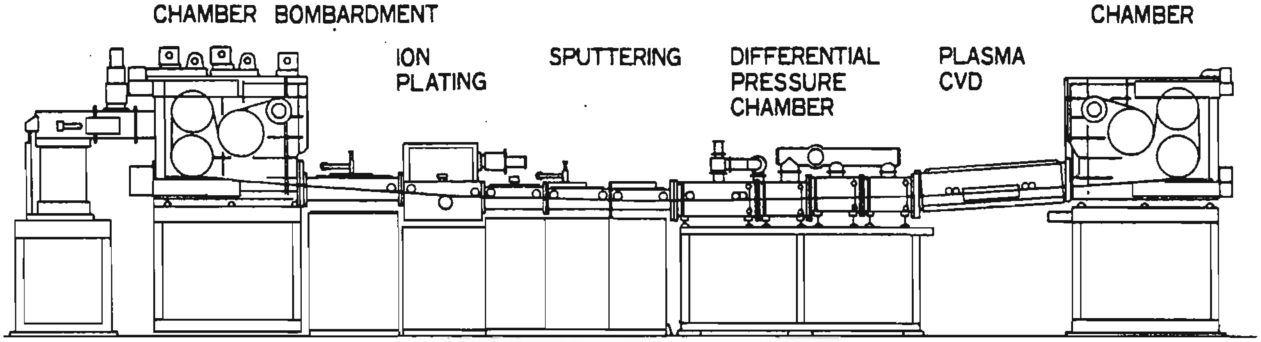


Figure 16. In-line dry coating process.

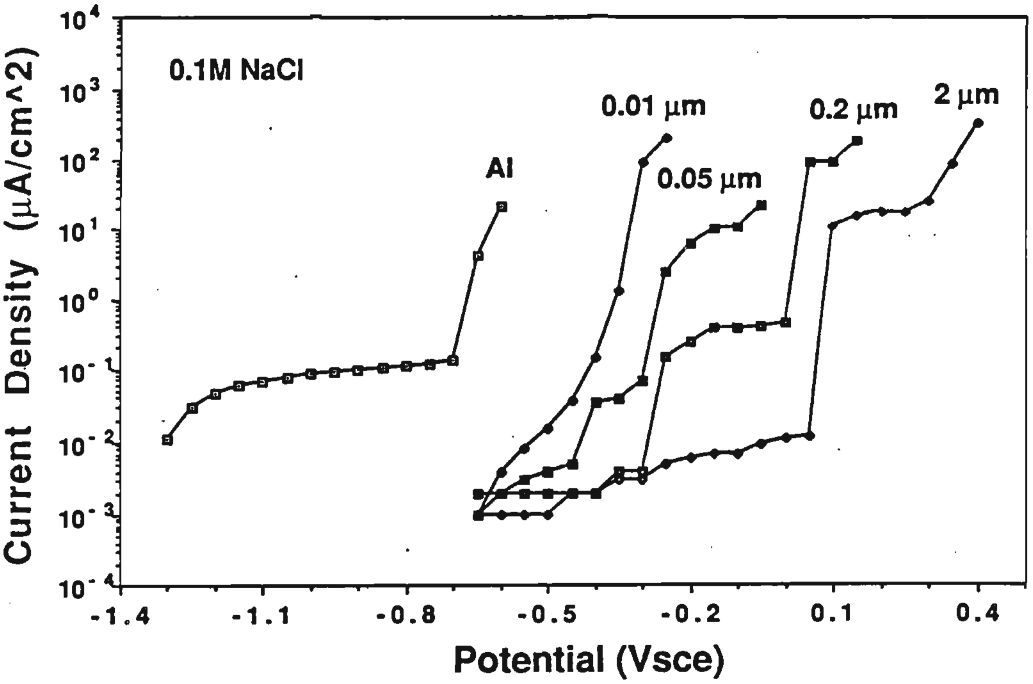


Figure 17. Anodic polarization curves for aluminum and aluminum with a number of IBAD coatings ranging from 0.01 to 2.0 µm.

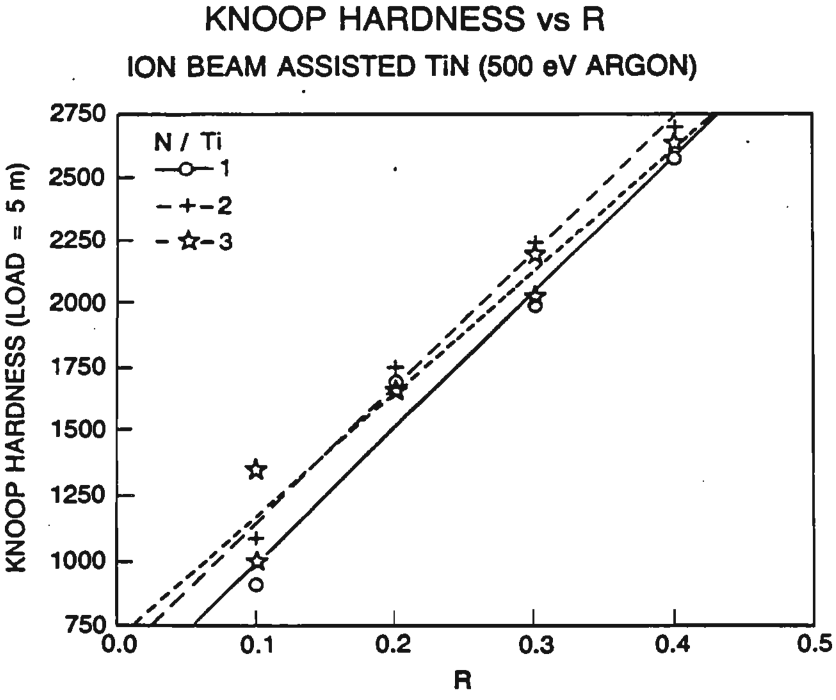


Figure 18. Hardness of IBAD TiN films vs. arrival ratio of Ar to Ti atoms.

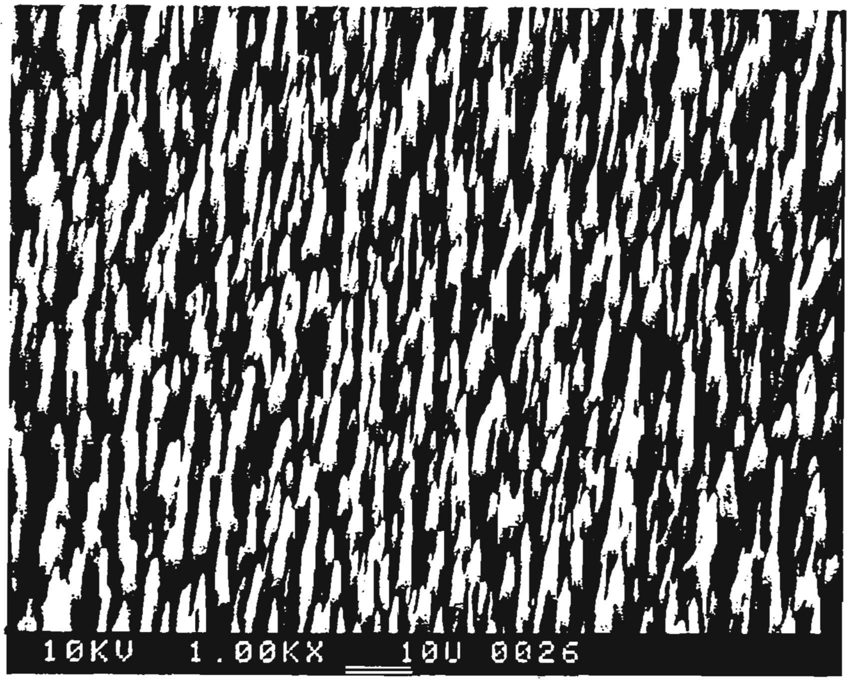


Figure 19. SEM photomicrograph of a textured carbon surface on an oven-fired high conductivity (OFHC) copper substrate. The angle with the surface is 30°, the processing time is 3 h at 5 mA/cm^2, and a 10-μm scale line is indicated on the title block.

17. A SUMMARY OF CRITICAL ISSUES FOR APPLICATION OF ORGANIZED MOLECULAR ASSEMBLIES AT SURFACES

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I. INTRODUCTION

The subject of ultrathin ($\sim$ 1-10^3 nm) organic films has become of considerable interest over the past decade because of a few existing and many potential technological and scientific applications [1]. The understanding of these materials is usually very incomplete when extrapolations are made from the behavior of bulk phases, because interfacial phenomena, of little concern in bulk material properties, can profoundly affect the behavior of ultrathin films. In addition, specialized procedures, designed specifically for ultrathin film synthesis, often cannot be adapted to bulk materials synthesis, and thus some materials structures and phases can only be obtained in film form. Because of these facts, it is necessary to view ultrathin organic films as generating their own unique materials issues with regard to potential and present applications.

One particular class of film structures for which the above points are most certainly true is highly organized molecular films or organized molecular assemblies (OMAs). The term "highly organized" refers to the spatial organization of the molecules. In the limit of perfect translational and orientational ordering, the molecules form a single crystal, which can be two- or three-dimensional, depending on whether one or more layers of molecules are present, respectively, and also whether or not the important degrees of freedom of the system exist exclusively in the surface plane or include the out-of-plane direction. As the extent of translational and orientational correlations decrease, the limit of complete disorder is reached, and the molecular assembly is no longer organized, in the sense used in this discussion. Different types of highly organized films can exist. For example, it is common to have low translational order films in which high orientational order exists (quasicrystals). These latter structures are generally considered highly organized also. Thus the term "highly organized" is somewhat arbitrary, and indeed, to characterize a given film as organized, one must, to be rigorous, state quantitative correlation parameters such as correlation decay lengths and orientational order parameters.

The general properties of highly organized ultrathin films that are of the greatest interest for applications are (1) high packing densities with low defect concentrations, (2) molecular alignment, (3) the capability of synthesizing surfaces with tailored physical and chemical properties, especially in selected spatial patterns, and (4) flexibility in selecting the types of molecular functionality and structural units present. Other properties such as thermal and photochemical stability are of interest, depending on the specific application.

To actually use these types of films, a number of unresolved issues must be confronted. Is it possible to design a desired specific architecture and successfully synthesize the structure, or are present capabilities limited? Given a successful synthesis, will the structure actually perform its function? Is the given structure a stable, minimum energy structure, or will it revert in time to another more stable form? There are a number of other similar issues that one can formulate. In the next section, a number of these issues are presented.

A number of critical issues center on film preparation. At present, there are two major preparation methods for organized ultrathin film structures, Langmuir-Blodgett (LB) and self-assembly (SA), and films can be conveniently classified according to which of these two methods was used to generate the film. The LB procedure consists of a specialized dip-transfer process of a monolayer film, preorganized on a water surface, from the water to a substrate. Repeated transfers result in multilayer films. The subject of LB films has been extensively reviewed [2-4], and will not be reviewed here. The SA method has become very popular, mostly for scientific study, in the past decade. In this method, a substrate surface is covered by a monolayer of molecules by simply exposing the substrate to a solution (or less often vapor) of the molecules. The process occurs spontaneously, and often, strong chemical bonding to the surface occurs at specific sites. The bonding can occur in an arrangement that will give rise to crystalline films. Almost always, multiple layers must be prepared by chemical coupling strategies. A recent review of SA films is available [4]. The following section will assume that the reader is familiar with the details found in the above references and other readily available current literature.

II. CRITICAL ISSUES

A. Critical Properties of OMAs for Potential Applications

In Table 1, a list of critical properties affecting various applications is presented. Other critical properties and applications can be considered, but for purposes of simplifying the discussion, the list is limited to fairly common issues. The nature of the properties listed needs to be defined in some detail.

Defects are classified into random defects, such as large patches of missing films ($\geq$ 0.1-1.0 μm), small patches of missing films that are termed pinholes ($\leq$ 0.1-1.0 μm), and defects in more smoothly varying density fluctuations arising from long-range structure correlations such as grain boundaries and modulation between amorphous and ordered films regions, as well as other film structure subtleties such as hollow regions in cyclic molecules.

Surface activity refers to the ambient (outer) film surface properties of chemical activity, including acidity and basicity; wetting properties such as hydrophobicity, olephobicity, and hydrophilicity; and combinations that can lead to biological activity.

The substrate/film interface is viewed in terms of the specific chemical bonding that may exist to bind the adsorbate to the substrate and the nature of the charge distribution and electronic states at the interface, which can be very important for semiconductor electronic devices.

The electrical and electronic structure of the film concerns the distribution of charge, usually in the form of permanent dipoles, the presence of polarizable electrons, and low lying excited states. Of particular interest in this category is the directional or orientation dependence of the above features with respect to electrical and electromagnetic excitation. The active features, such as dipoles, must be aligned along favorable orientations. Also the inversion symmetry of the distribution of charge or polarizability elements in the film is important. For example, second harmonic generation of light can be induced by the bulk of a film only when the film symmetry is properly noncentrosymmetric (no center of inversion symmetry for the structural repeat unit).

The stability of the film is an obvious practical consideration in applications. Thermal and chemical stability are necessary for most exposure environments. Chemical stability can include reactions with O_2, H_2O and other specific chemicals, as well as perhaps a more physical property, stability towards desorption in the presence of solvents. In the case of optical devices, photostability may be important,

Table 1. Critical Properties of Organized Molecular Assemblies for Potential Applications

	Defects		Surface Activity		Substrate/Film Interface		Electrical and Electronic Structure		Stability				
Potential Application	Pin Hole	Long-Range Structure Correlations	Chemical Activity	Wetting	Bonding	Electronic State	Orientation	Film Symmetry	Thermal	Photo	Chemical	Particle Beam	Multilayer Capability
<u>Devices</u>													
<u>Electronic</u>													
Chemical sensors	X		X	X	X	X	X				X		
Photovoltaics	X				X	X	X	X	X	X			
Microlithography	X								X	X	X	X	X
<u>Electrochemical</u>													
Chemical sensors	X		X	X	X	X	X	X			X		
Photochemical	X		X		X	X	X	X		X	X		
Synthesis	X		X		X	X	X	X			X		
<u>Optical</u>													
Photonic switches (nonlinear)		X					X	X		X			X
Electrooptical	X						X	X		X			X
Displays	X						X	X	X	X			X
<u>Coatings</u>													
Diffusion barrier	X			X	X				X		X		X
Anticorrosion	X			X	X				X		X		X
Antiwear					X				X				X
Bioactive			X	X							X		
Specific wettability		X		X	X						X		
Adhesion coupling agents			X	X	X				X		X		

and in the case of microelectronic processing and lithography resist applications, photo or particle beam stabilities may be desired or not, as the case may be for a given process step.

Finally, many applications require substantial film thickness, which in turn requires the film synthesis process to have multilayer capability in order to stack many layers of molecules into a stable, organized structure, a severe challenge in many cases.

The central points for discussion here are: what are the varieties of applications envisioned and what critical properties must be controlled for successful engineering? After these properties are identified, the question of how to control them arises.

B. Preparation Variables, Critical Properties, and Potential Applications of OMAs

Table 2 relates critical film properties to the preparation variables, substrate, film materials, and processing method. For many applications, there may be very little leeway in selecting different substrates or film materials, and then the processing method is considered the major variable. A fairly common situation is that the substrate is fixed. For example, to fabricate a specific molecular-based electronic device, the only semiconductor material possible may be GaAs, but the film material and processing offer flexibility. However, even for a fixed substrate material, there is usually additional flexibility with regard to the substrate, particularly the degree of surface preparation, which includes cleanliness, roughness, chemical preparation to generate active bonding sites, choice of particular crystal faces that determine lattice geometry, and the degree of control in minimizing lattice defects. The choice of film material critically depends on the nature of the film property needed, obviously, and also upon the strategy developed to form the film structure. The organic molecular structures that can be chosen almost appear infinite, but actually they can be conveniently divided into several simple categories derived from the constraints of the narrow range of processing methods available. The major category, which has been used almost exclusively for organized films, is amphiphilic molecules. These are molecules with a hydrophobic (water insoluble) and a hydrophilic (water soluble) portion, and all surfactants are based on this structure. A typical surfactant structure consists of a long alkyl tail (~ 12-20 carbon atoms) and a water soluble head group (ionic or hydroxylic group).

Almost all LB-processed films are based on surfactants, and the degree of amphiphilicity is a critical parameter affecting the film quality. LB films also can be made from highly water insoluble molecules with no hydrophilic portion, but good quality organized films have resulted in only a few cases, and the procedures are difficult [3]. In most cases of LB films, the head group is attached to the substrate by weak physisorption forces, a characteristic that can lead to poor thermal and solvent stability.

Poor thermal and solvent stability can be improved by the use of polymeric molecules produced either by deposition of preformed polymers or by postpolymerization of monomeric films. These characteristics can also be improved by the presence of strong chemical bonding of the film to the substrate. This characteristic requires functional group reactivity with the substrate. Such a situation is obtained with SA films, because it can be easily arranged to use substrates whose chemical propensity to react with selected functional groups drives the assembling of the adsorbate molecules. Regardless of whether the head group is bound at the surface by physisorption or bond-specific chemisorption, the shape of the constituent molecule plays a critical role in determining film properties. For example, if the lattice geometry of active bonding sites for a given substrate requires that the molecules in a SA monolayer be bound together in an organized geometry conflicts with that allowed by the molecular size and shape, then the film can never have as high a translational ordering as the substrate lattice. In addition, molecules with symmetrical shapes, e.g., rod-like (common for most surfactants), can lead to very dense packing, whereas highly asymmetric or cavity-containing molecules will pack at lower densities with a more porous

Table 2.
Preparation Variables Which Affect Critical Properties of Organized Molecular Assemblies

	Critical Property of Film												
	Defects		Surface Activity		Substrate/Film Interface		Electrical and Electronic Structure		Stability				Multi-layer Capability
Preparation Variable	Pin Hole/ Patch	Long-Range Structure Correlations	Chemical Activity	Wetting	Bonding	Elec-tronic State	Orien-tation	Film Symmetry	Thermal	Photo	Chemical/ Solvent	Particle Beam	
1. Substrate	X	X		X	X	X	X	X	X		X	X	X
Roughness	X	X		X			X	X					X
Cleanliness	X	X			X	X			X		X		X
Active bonding sites:													
Lattice geometry		X					X						
Lattice defects	X	X		X									
Chemical nature					X		X		X		X		
2. Film Material	X	X	X	X	X	X	X	X	X	X	X	X	X
Amphiphilicity	X	X		X									X
Functional group reactivity with substrate	X	X		X	X	X			X		X		
Shape	X	X		X			X						
Multifunctional molecule			X	X			X			X	X	X	X
Polymeric molecule	X	X		X			X	X	X		X	X	X
3. Processing Method	X	X	X	X	X	X	X	X	X		X		X

structure at the molecular scale. Control of the latter porosity is a critical feature in films that regulate charge or mass transport, such as electrochemical electrode coatings and diffusion barrier films.

For many applications, the synthesized film must contain one or more specific molecular groups at specific locations in the film to achieve the desired function of the structure. Three generic examples of the need for multifunctional molecules in a film structure are (1) for nonlinear optical (NLO) devices, highly conjugated, heteroatomic pi-electronic functionality usually needs to be located in the film interior, (2) for a surface of a specific controlled wettability, a specific type of functional group, (e.g., an OH group), needs to located at the film surface, and (3) for an electrochemical sensor, a surface bound group that specifically binds a target analyte is often desired to achieve high chemical specificity for the device.

The discussion above points out the general connections between processing variables and applications properties. In Table 3, some examples of specific connections are given for selected generic classes of applications. Without a highly specific target application object or item, it is not possible to bring out these connections in real detail. Rather, the entries in Table 3 are designed to show the types of connections that one should consider.

C. Major Techniques for Characterizing Critical Features of Molecular Films

Characterization is a major capability whose degree of realization can act as a gate to control success in making structure/function correlations, but often remains a hidden factor in the advancement of thin-film technology. For this reason, techniques that have been successful in characterizing structural features of organized molecular films are made part of this discussion and are presented in Table 4. It is this author's opinion that X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and infrared (IR) spectroscopy are the most cost-effective tools for characterizing critical aspects of molecular film structure. However, it is clear to workers in this field that these three techniques cannot cover all critical features, for example, translational ordering, and that a combination of techniques is needed in each film analysis. A further point is that different techniques may give apparently conflicting information because of the lack of accurate interpretation of complex data or spectra, particularly in a quantitative fashion. Having noted these problems, we return to the central issue of controlling the final properties by control of the synthesis.

D. Important Film Characteristics for LB and SA OMAs

In Tables 5 and 6, a very abbreviated tabulation of important film characteristics is given for each of the two major processing methods [4-9]. For detail, particularly on LB films, reference texts should be consulted [2-4]. The major features of LB films in an encapsulated summary are: (1) excellent multilayer capability, (2) extreme, but not complete, limitation to surfactant molecules with no capability for multifunctional polar, hydroxylic groups, (3) low thermal and solvent stability except for the very limited cases of pre- or postpolymerization of the film molecules, and (4) excellent, low defect crystalline films for some rod-like surfactant molecules. Most of the early work, actually until the past half decade or so, has been done with LB films. Recently, with the discovery of new SA film/substrate systems, the field of SA films has expanded at an accelerating pace. Table 6 presents the major SA films systems and associated pertinent features. SA films differ markedly in two respects from LB films.

The first difference is that whereas, in general, preparation of any LB film is independent of the particular substrate material, in contrast, the very existence of most SA films is dependent on specific chemical interactions between a specific functional group on the film molecule and specific sites on the substrate surface. In some cases, the interactions are very weak (e.g., weak hydrogen bonding) and as a result, film stability toward heat or solvents will be poor. However, in the cases of many SA films

Table 3. Selected Examples of Optimal Materials and Processing for Specific Target Applications

Selected Application	Possible Major Requirements	Optimum Processing Method	Optimum Materials	
			Substrate	Film
Open gate, chemically sensitive FET	Surface chemical activity; monolayer; substrate/film bonding and electronic states; thermal and chemical stability; low defects; protective barrier for semiconductor surface degradation	SA	Semiconductor, periodic lattice of bonding sites	Multifunctional with substrate bonding group; specific placement and orientation of functional groups
Modified Schottky diode	Monolayer; specific substrate/film interface bonding; charge distribution and electronic states; thermal stability; pinhole defect-free; damage resistance toward metallization	SA	Semiconductor, periodic lattice of bonding sites	Multifunctional with substrate bonding group; presence of charge separation or polarizable groups
Electrochemical sensor	Surface chemical activity; monolayer; substrate/film bonding; chemical/solvent stability; preselected defect channels for charge transport; redox active groups	SA	Conducting material, periodic lattice of bonding sites, non-corrodible	Multifunctional with substrate bonding group; molecular shape to allow transport channels; redox functional group
Photonic switch	Multilayers (~ 1 μm); electronic structure with high nonlinear optical response and appropriate inversion symmetry; density fluctuation-free; photostability	LB-multilayer deposition	Optically transparent, highly smooth, inert to water	Highly amphiphilic; nonlinear optical group aligned along selected molecular axis; liquid crystalline
Diffusion barrier coating (e.g., H_2O, O_2)	Dense, defect-free packing; thermal and solvent stability	LB-multilayer deposition	Smooth, inert to water	Highly crystallizable molecule; possibly crosslinkable; amphiphilic or water insoluble and stiff
		SA	Availability of dense surface bonding sites; periodic preferable	Oligomeric or polymeric molecules with substrate bonding group; or small molecules that densely pack
Adhesion coupling layer	Surface chemical activity; substrate/film bonding; thermal stability	SA	Available surface bonding sites	Multifunctional with substrate bonding group and surface chemically active group
Antiwear film	Low surface wettability (low surface energy); substrate/film bonding; high thermal stability; uniform coverage	SA	Available surface bonding sites	Substrate bonding group; low surface energy groups; flexible linkages; thermal stability; possibly oligomeric or polymeric

Table 3. Selected Examples of Optimal Materials and Processing for Specific Target Applications (Concluded)

Selected Application	Possible Major Requirements	Optimum Processing Method	Optimum Materials	
			Substrate	Film
Bioactive coating	Surface bio(chemical) activity; thermal and chemical stability; substrate/film bonding; dense packing to support surface orientation and arrangement	SA	Available surface bonding sites; noncorrodible	Multifunctional; substrate bonding group; possibly a combination of functional groups or separate molecules that can arrange in a cluster to form a site with high chemical or biospecificity
Nano-lithography resist	Specific sensitivity to degradation or crosslinking by photon or particle beams; specific solvent stability; thermal stability; low patch defects	SA	Available surface bonding sites, preferably periodic	Multifunctional; surface bonding group; radiation sensitive linkages; plasma resistant groups; possibly polymeric or oligomeric for uniform coverage
		LB-multilayer deposition	Smooth, inert to water	Containing cross-linkable or radiation degradable groups; crystallizable molecule

Table 4. Major Techniques to Characterize Critical Aspects of Film Structure

	Characterization Technique														
Critical Film Feature	XPS	SIMS	IR	Ellip-sometry (including SE)	RBS	SEM	AFM, STM (TEM)	XRR, XRD	He Scat	SFG	HREELS	UPS	Raman	ISS	LEED, (TED)
1. Film Coverage															
Total coverage/thickness	X		X	X	X			X							
Patch defects (> 0.1-1 μm)	X	X			X	X	X							X	
Chemistry				X				X							
2. Elemental Composition															
Average	X				X										
Surface	X													X	
Depth profile (including sputtering and nondestructive)	X				X									X	
Image (lateral)	X													X	
3. Molecular Groups															
Chemical bonding	X	X	X							X	X	X	X		
Orientation	X	?	X	X			X(?)			X	X	X	X		
Conformations		?	X							X		X	X		
Average composition	X	X	X							X	X	X	X		
Depth profile composition	X	X(?)		X	X					X(?)		X		X	
Composition image (lateral)	X	X													
Electronic states	X			X								X			
4. Ordering/Defects															
Pinhole defects (< 0.1-1 μm)	X	X				X	X							X	
Long range translational; density fluctuation defects			X				X	X					X		X
Orientational ordering			X	X			X	X					X		
Surface ordering							X(?)		X	X					

Table 4. Major Techniques to Characterize Critical Aspects of Film Structure (Concluded)

	Characterization Technique														
Critical Film Feature	XPS	SIMS	IR	Ellipsometry (including SE)	RBS	SEM	AFM, STM (TEM)	XRR, XRD	He Scat	SFG	HREELS	UPS	Raman	ISS	LEED, (TED)
5. Substrate/Film Interface															
Chemical bonding	X	X(?)	X	X						X	X	X	X		
Pinning geometry							X	X							X

Definition of Acronyms for Characterization Techniques

XPS	X-ray photoelectron spectroscopy
SIMS	secondary ion mass spectrometry
IR	infrared
SE	spectroscopic ellipsometry
RBS	Rutherford backscattering spectroscopy
SEM	scanning electron microscopy
AFM	atomic force microscopy
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
XRR	X-ray reflectometry
XRD	X-ray diffraction
He scat	helium scattering
SFG	sum frequency generation
HREELS	high resolution electron energy loss spectroscopy
UPS	ultraviolet photoelectron spectroscopy
ISS	ion scattering spectroscopy
LEED	low energy electron diffraction
TED	transmission electron diffraction

Table 5. Important Film Characteristics Possible from Processing Methods

Processing Method	Important Film Characteristics								
	Defect Content			Polar, Multi-functional Molecules for Chemical and Wetting Surface Activity	Thermally, Chemically Stable Films	Chemically, Electronically Controlled Substrate/Film Interface	Multilayer Capability	Polymeric Films	Unusual Substrate Geometry
	Patch	Pinhole	Long-Range Density Fluctuations						
Langmuir-Blodgett	Can be made very low under dust-free conditions with clean substrates	Can be made very low by use of clean substrates	Uniform, high density for surfactant-type molecules; large-area single crystals possible (>> 1 μm); shaped molecules (cylinder) can give controlled pores; e.g., calilxaranes	Chemical flexibility very limited; molecules must form uniform films on water (although Hg, highly self-associated, hydroxylic organic liquids and other similar liquids are possible); only highly water insoluble molecules work, surfactant structures best; usually only one Bronsted acid-base group allowed, but multiple non-polar groups (e.g., vinyl) are possible; the latter can be used to crosslink films after formation	Lack of substrate bonding gives poor thermal and solvent stability; this can be somewhat overcome by polymeric films	Secondary, coincidental result in a few cases; usually not possible because of aqueous processing disturbing substrate surface chemistry and because of lack of substrate/film chemical bonding spacing consistent with LB film packing arrangement	Excellent; possible to do A-B A-B or A-B B-A stacking of rod molecules to control inversion symmetry for electrical or nonlinear response	Uniform polymer films possible by direct preparation using surfactant polymers or stiff aromatic polymers (e.g., polyimide); post-cross-linking possible for some surfactant molecules containing vinyl and propargyl groups	Poor; uniform coverage only on smooth, low radius of curvature surfaces

Table 5. Important Film Characteristics Possible from Processing Methods (Concluded)

Processing Method	Important Film Characteristics								
	Defect Content			Polar, Multifunctional Molecules for Chemical and Wetting Surface Activity	Thermally, Chemically Stable Films	Chemically, Electronically Controlled Substrate/Film Interface	Multilayer Capability	Polymeric Films	Unusual Substrate Geometry
	Patch	Pinhole	Long-Range Density Fluctuations						
Self-assembly	Can be made extremely low using clean substrates; dust should not be a problem	Can be made very low using clean substrates	Large-area single crystals possible using single-crystal substrates with low defect contents (e.g., MBE substrates)	Chemical flexibility very good; require selective substrate chemistry based on hard-soft donor-acceptor interactions to selectively bind one group leaving others free; molecules must be volatile for gas-phase assembly or soluble or molten for liquid-phase assembly; solvents used must not corrode substrate.	Substrate bonding can lead to highly stable films—thermally stable to > 200°C possible with excellent solvent resistance; cross-linking during formation (e.g., siloxanes) gives high stability without surface bonds	Using O_2-free and H_2O-free conditions, substrates can be chemically prepared for organometallic bonding reactions (e.g., bare semiconductor surfaces—oxide-free); bonding can cause specific permanent charge redistribution at the substrate interface	Poor; requires laborious sequence of chemical surface modification, followed by coupling of next layer; special strategies needed to avoid defects	Strong surface bonds tend to kinetically trap polymer conformations and chain configurations in nonequilibrium frozen glasses—porous structures result	Any shape works because molecules are carried to the surface by molecular diffusion; however, high radius of curvature means high index crystal planes are present and overlayer structures become poorly ordered

Table 6. Survey of Stable, Highly Organized, Self-Assembled Monolayer Systems

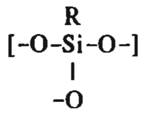
Substrate	General Type of Absorbate Molecule	Substrate/Film Bonding	Types of Multi-functionality Allowed	Characteristics of Film		Potential Applications	References
				Physical	Chemical		
SiO_2 (amorphous glass or native oxide)	X(CH_2) $SiCl_3$, usually n = 18	1. Quasi-2D polysiloxane network forms  $\overset{R}{[-O-\underset{-O}{\underset{\vert}{Si}}-O-]}$ 2. Occasional Si-O-Si bonds form at surface -OH sites	X ≡ CH_3, CO_2CH_3 CH = CH_2, Br, CN are typical; a variety of soft donors and acceptors possible	Highly stable; low translational order; high orientational order with chain axis oriented close to 90° to surface	Chemical reactions can be carried out on X; formation of OH can lead to condensation of second layer and continued sequence to multilayers	Optical devices if high quality multilayers with NLO groups are formed; adhesion coupling layer	4
Al_2O_3 (native oxide)—also other hydroxylated oxides such as TiO_2, SnO_2, etc.	X(CH_2)$_n$ $SiCl_3$, usually n = 18	As for SiO_2	CH_3, CH = CH_2, CN	Presumably similar to SiO_2 (almost no characterization studies)	Presumably similar to SiO_2	Protective coatings; modified electrochemical electrode surfaces	4
Au	X(CH_2)$_n$SH, [X(CH_2)$_n$S]$_2$, n = 1-24 have been studied; also RSH where R = aromatic rings	Au-SR bond; bond angle with surface ~ 90°-120°; (√3 × √3) R30° overlayer on Au(111)	Highly varied, almost any hard donor, acceptor, or nonpolar group: OH, NH_2, CO_2H, CH = CH_2, CH_3, etc.	Thermal stability to ~ 200°C; high translational, orientational order with chain axis oriented ~ 64° from the surface for a Au(111) surface	Chemical reactions can be carried out on X; second layer can be formed by bonding of $RSiCl_3$ onto OH surface	Modified electrochemical electrode surfaces; bioactive surfaces	4-6
Au	X(CH_2)$_n$$SiCl_3$, usually n = 18	No chemical bonding to substrate, only polysiloxane network	Unexplored, should be same as for SiO_2	Highly stable thermally; higher translational, orientational order than for SiO_2	As for SiO_2	Modified electrochemical electrode surfaces	4

Table 6. Survey of Stable, Highly Organized, Self-Assembled Monolayer Systems (Continued)

Substrate	General Type of Absorbate Molecule	Substrate/Film Bonding	Types of Multi-functionality Allowed	Characteristics of Film		Potential Applications	References
				Physical	Chemical		
Au	$X(CH_2)_n\ S\ (CH_2)_mY$ $m,n \leq 20$	$\begin{matrix}R\diagdown\\R\diagup\end{matrix}S$ - Au bond; presumably σ donation ligand bonding	Similar to RSH, $(RS)_2$	Lower stability than RSH, $(RS)_2$ films; chain disorder suggests low translational order	Should be similar to RSH, $(RS)_2$ films except for lower solvent stability	Probably none because of low stability	4
Ag (Cu is similar)	$X(CH_2)_n\ SH$	RS-Ag bond; bond angle with surface apparently variable; incommensurate layer on Ag(111)	More limited than for Au since Bronsted Acid groups react with Ag(oxide) surfaces; non-hydroxylic such as CH_3, $CHCH_2$, CH, CO_2CH_3, etc.	Similar to Au, but chain axis is oriented ~ 78° from surface	Unexplored; probably less varied than for Au because Ag is more corrodible	Protective coatings; adhesion coupling layer	4,5,7
Ag	$X(CH_2)_n\ CO_2H^+$	$RCO_2^-Ag^+$ ionic bonding	Unexplored except CH_2; presumably nonpolar groups such as $CHCH_2$	Thermal stability unexplored; chains fully extended in a crystalline lattice and oriented near normal to the surface	Generally unexplored	Protective coatings; adhesion coupling layer	4
Ag	$X\ CH \begin{matrix}(CH_2)_m\text{-}CO_2H\\(CH_2)_n\text{-}CO_2H\end{matrix}$	As above	$X = -O-, -S-, \overset{O}{\overset{\vert}{-C-}}$, etc.	Thermal stability unexplored; "loop" structures form with surface dominated by properties of X; for $X \equiv H$ and $m + n = 30$, loops are arranged in a crystalline lattice	Unexplored; reactions of X may be possible	Protective coatings; adhesion coupling layer	8

Table 6. Survey of Stable, Highly Organized, Self-Assembled Monolayer Systems (Concluded)

Substrate	General Type of Absorbate Molecule	Substrate/Film Bonding	Types of Multi-functionality Allowed	Characteristics of Film		Potential Applications	References
				Physical	Chemical		
Al_2O_3	$X(CH_2)_n\ CO_2H$, n = 1-22 have been studied; other acid groups such as PO_3H_2, phenols are possible	$RCO_2^- Al^+$ (oxide) bonding	CH_3, $CH = CH_2$, $CH \equiv CH$; other non-polar or nonacidic groups possible	Thermally stable to ≤ 200°C; chain disorder for n ≤ 16 but more ordered for n ≥ 20; chain axis oriented ~ 75-78 degrees from surface	Generally unexplored	Protective coatings; adhesion coupling layer	4
GaAs	$X(CH_2)_nSH$	RS-As bonds presumed	CH_3 and hard donor acceptor groups such as CO_2H, CO_2CH_3, OH, etc.	Thermally stable < 200°C; chain ordering for n = 18	Generally unexplored	Modification of GaAs devices	9

(Table 6), strong ionic and covalent bonds impart considerable stability. Thus an important task associated with building a given type of film on a selected substrate is to find a suitable and specific substrate/functional group pair with appropriate chemical affinity. One apparent exception to this rule is the case in which the SA film is highly cross-linked, for example, in monoalkylsiloxane monolayers on inert substrates such as gold (Table 6) for which no chemical linkages to the substrate exist, only weak dispersion forces, and the stability is due to the insolubility and involatility of the polymerized monolayer. However, such films are still less stable than nearly identical films on a substrate such as SiO_2, which can form occasional bonds to the film via substrate silanol-film silanol condensation.

The second important difference between LB and SA films is that whereas LB multilayer films can be readily formed by repeated dipping SA monolayers, in contrast, represent the completion of the specific substrate/molecule assembling chemistry, and further layers must be formed by specific chemical coupling steps. Innovative, complex schemes for such multilayering have been reported, and three examples are given in Table 7. The first, the use of terminally substituted alkyltrichloro silanes, has been the traditional method [4], but recent unique methods, using zirconyl phosphonate chemistry [10] and amine alkylations combined with other coupling sequences [11], have recently been reported.

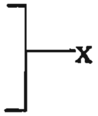
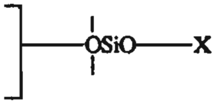
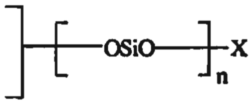
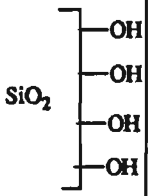
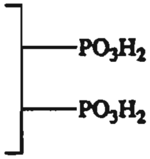
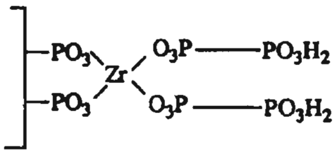
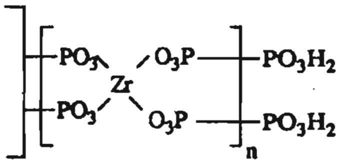
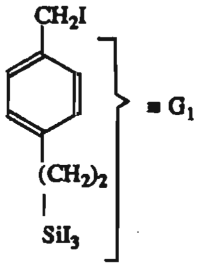
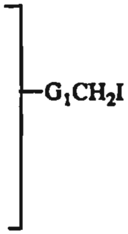
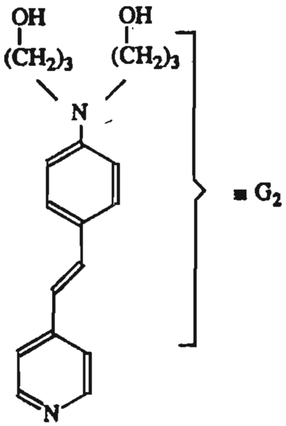
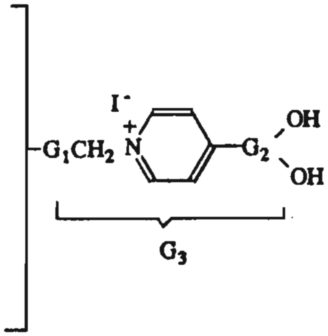
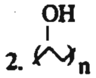
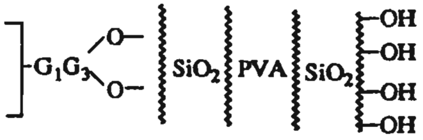
III. DIRECTIONS FOR FUTURE DEVELOPMENTS

There are two major directions for future work. The first is the exploration of applications for highly organized films. In this process, problems will be encountered in designing and carrying out syntheses of films that exhibit the desired functions. These problems will lead to both the refinement of current critical issues and the definition of new critical issues dealing with synthesis/structure/function correlations. The second direction for future work is the scientific study of the most important of these critical issues.

The most important needs in the field of organized films are to develop or establish

- Quantitative methods for characterization, particularly film defects
- A relationship between film structure, molecular pinning site geometry, and the adsorbate molecule in SA films
- Theories relating wetting properties to surface molecular structure
- Synthetic protocols to make highly patterned, multifunctional surfaces
- Controlled pore size and pore distribution films
- Stable SA monolayers based on specific molecule/semiconductor surface chemistry for the major semiconductor materials including GaAs, Si, Ge, and InP
- Multilayer film synthesis strategies to provide low defect, highly oriented superlattice structures.

Table 7. Strategies for Constructing Multilayer Film Structures Using Self-Assembly and Chemical Coupling Starting with an SiO_2 Surface

	First Layer		Second Layer		Third and Additional Layers	
	Reagent	Film Structure	Reagent	Film Structure	Reagent	Film Structure
	X $\vert$ $SiCl_3$		1. Convert X→OH 2. X $\vert$ $SiCl_3$		Repeat second layer steps n-1 times	
	PO_3H_2 $\vert$ $Si(CH_3)_2$ OH		1. $ZrOCl_2$ 2. PO_3H_2 $\vert$ PO_3H_2		Repeat second layer steps n-1 times	
					1. $(Cl_3SiO)_2SiCl_2$ 2.  PVA 3. $(Cl_3SiO)_2SiCl_2$	 - Repeat third layer steps for thicker SiO_2/PVA layers - Repeat first and second layer steps for another GaG$_3$ layer - Repeat all steps for complete repeating multilayer structures

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18. STATUS OF SURFACE MODIFICATION FOR MINIMIZING DIRT RETENTION: ORGANIZED MONOMOLECULAR ASSEMBLIES

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ABSTRACT

Soiling significantly hinders the cost- and energy-effective deployment of many surfaces used in solar technologies. Because soiling expresses the universal, irresistible drive toward lowest surface free energies, preventive technology will logically be directed toward reducing surface energy and physical roughness while maintaining desired bulk and optical properties. Surface modification with fluorinated ultrathin oriented films (Langmuir-Blodgett films or self-assembled monolayers) has been demonstrated to hold promise for this application.

I. INTRODUCTION: SOILING AND SOILING RESISTANCE

A. Soiling as a Generic Problem

Mittal has pointed out that "people dealing with surfaces are afflicted with molysmophobia[1], and rightfully so" [1]. Dirt retention on surfaces, known also as soiling, fouling, contamination, and a host of more colorful, less scientific, and occasionally unprintable terms, is an energy-consumptive, cost-enhancing problem that exerts continuing negative impact on every technology. Recent years have brought increased attention to its cost, giving rise to extensive applied and fundamental research, to current-awareness journals like the Fouling Prevention Research Digest and to conferences such as the 1990 Conference on Biofouling at SUNY–Buffalo and the quadrennial International Conferences on Fouling and Cleaning in Food Processing.

B. Soiling as a Problem for Solar Energy Technologies

Soiling is of particular concern when operations rely on stable, optimized performance of a solid/fluid interface, like the interface between a heliostat and ambient air. Heliostats, whether silvered glass or the newer silvered-polymer membranes, incorporate many interfaces, each with its special susceptibility to soiling and degradation. The compromise of each interface exerts a unique influence on the efficiency of the total unit. The first surface is the most susceptible, because it must confront the synergistic actions of ultraviolet light, atmospheric gases like oxygen and water vapor, varying temperatures, and bombardment by a wide variety of soilants that can cause both physical and chemical degradation.

Figure 1 is a highly magnified schematic of a "worst-case" reflector surface, with no particular attention given to relative scale or to material of composition. Because the glass or polymer portions of many reflectors are insulators, they tend to build up electrons at the interface. Because some potential soilants bear positive charges, they are electrostatically attracted to reflector surfaces. Other soilants may

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[1] Molysmophobia: fear of dirt or contamination, from Mrs. Byrne's Dictionary of Unusual, Obscure, and Preposterous Words, University Books, Secaucus, NJ, 1974, as cited in Reference 1.

be attracted by long-range forces and attach by combinations of physical adsorption and chemisorption, as discussed below.

From a macroscopic point of view, this reflector surface is undoubtedly very smooth; it may even be microscopically and optically smooth. However, no mechanical polishing, chemical treatment, etching technology, sputtering, or polymer-casting technique can produce a surface that is smooth on a molecular scale. Even a very large molecule, the smallest entity that could be defined as "dust" or "soil," will perceive this surface as rough, with cracks and crevices of widely varying shapes, sizes, and depths. Such irregularities offer sites for soil particles; given fortuitous matching of irregularities, "lock and key" adhesion may render even small particles virtually impossible to remove, despite the lack of an "energetic" reason for their permanent attachment.

The Solar Energy Research Institute has stated that "short-term specular reflectance losses of Ag/glass mirrors are from 0.5% to 1.0% per day at the Sandia site, with losses approaching asymptotic values of 19% in 1.8 years. Short-term power losses of photovoltaic modules, attributed to soiling, are 4% to 7% per month, approaching asymptotes of 25% to 60% for periods of greater than 1 year, depending on site and season. The loss of power produced in central receiver concepts is roughly twice that of the loss in reflectance of the heliostats; therefore, eliminating soil from reflecting elements is a necessary condition for optimum performance of such a system . . . present first and second mirror materials do not last for the time periods required for cost-effective concentration of solar energy" when exposed to the real environment [2]. Czanderna has said that "our ability to prepare interfaces with the desired performance properties that will also retain stable performance will be critical (present author's underlining) in the reliable deployment of [solar energy conversion] technologies" [3].

Roth and Pettit [4] and Clark et al. [5] supported Czanderna's evaluation [3] with their results from studies of silvered-glass mirrors at Albuquerque, NM [4], and various cover plate materials at New River, AZ, Miami, FL, and Gaithersburg, MD [5]. Figure 2 reproduces Roth and Pettit's diagram of projected reflectance changes for the cases of "ideal" mirror cleaning, washing in which cleaning agents cause degradation, and long- and short-term soiling in the absence of any cleaning. Figure 3, from the same study, shows actual specular reflectances of glass mirrors undergoing soiling-cleaning cycles of various lengths. "The average daily reflectance loss for, respectively, the 2-, 6-, and 12-day cycle mirrors was 0.0085, 0.0061, and 0.0051 reflectance units. Thus, the rate of dust accumulation decreases as the amount of accumulated dust increases" [4]. Moreover, "net scattering by the accumulated particles increases with decreasing wavelength and with increasing level of soiling" [4].

C. Cost, Energy, and Environmental Benefits of Modification

SERI has said that reflector cleaning constitutes a large fraction of the lifetime cost of operating a [future] solar thermal power plant. The logical solution is to render mirror interfaces permanently adhesive so that they repel soilants throughout their lifetimes. There are associated indirect benefits: heliostat cleaning with strong reagents like aqueous solutions of hydrofluoric acid and surfactants is a serious source of environmental concern. Minimizing the use of cleaning agents would benefit the environment as well as the dollar-and-energy-cost package.

An optimized antisoiling technology would find alternative applications in optical devices and instrumentation manufactured from transparent or reflective polymers and glass. Soiling and fouling also compromise operations in many diverse fields, including the critical industrial operations of separations and heat transfer. These consume vast amounts of energy that could be substantially reduced by strategic minimization of soiling and fouling.

II. SOILING-PREVENTION DESIGN PARAMETERS

A rational approach to soiling prevention by surface alteration must take into account at least the following practical considerations:

- Performance-related cleanliness criteria
- Maintenance of applications-related bulk and surface properties
- The driving forces behind soiling
- Cost, energy, and environmental analysis of modification.

A. How Clean is Clean Enough?

Although we speak freely about "maintaining" cleanliness, a clean or adsorbate-free surface is in fact a rarity in the real world. According to Morrison, "There are three types of contamination that must be removed in order that the results can be described as representing a clean surface. One is a separate phase, such as an oxide on a metal. The second is adsorbed gases and impurities. The third is crystal damage, including implanted ions near the surface. The problem of crystal damage arises particularly when sputtering is used to clean the surface" [6]. By these criteria, we may postulate that clean surfaces were never available until it became possible to prepare and maintain, for at least a limited time, single-crystal surfaces by cleavage in a vacuum of $< 10^{-9}$ Torr, or by ion bombardment and annealing cycles.

Fortunately for solar energy technologies, the definition of "clean" is not nearly this stringent: a clean solar technology interface is simply one that retains the performance properties for optical surfaces, such as refractive index, specular reflectance, absorption, reflectivity, and transmittance for optical surfaces, that characterized it prior to exposure under use conditions. Nevertheless, implementation of even this limited objective has proved challenging.

B. Origin and Experimental Assessment of Adhesive (Soiling) Capability

1. A Schematic of a Soiled Surface

Eirich commented in 1967 that "there are no free, or pure, surfaces in nature. Every so-called surface, in actuality, is an interface between two physically recognizable phases and is covered spontaneously with a hierarchy of adsorbed layers such that the free surface energy becomes minimized" [7]. Patrick labeled Eirich's scheme the "Hierarchy of Spontaneously Adsorbed Layers" and named the first monolayer the "A" film, characterized by such strong adsorption to the virgin or atomically clean surface that it can be removed only through literal destruction of the interface (Fig. 4) [8]. An A film potentiates strong attachment of B-layer soilant, removable by energy-intensive chemical and mechanical procedures such as scrubbing with a surfactant solution. B-layer soilant, in turn, invites relatively loose attachment by C soil, which is quite chaotically arranged and can be removed with minimal energy input, for example. by shaking or evacuation to facilitate desorption.

This schematic points up important issues: the apparently irresistible drive of most surfaces to form new interfaces by sorbing A layers; the impossibility of removing an A layer, once established; and the fact that A layers usually, if not always, potentiate the buildup of B and C layers.

2. Energies and Rates of Substrate—Adherend Interactions

Roth and Pettit observed that "The initial forces of adhesion are probably dominated by electrostatic forces and surface energetics, while after sufficiently long periods of time, stronger chemical and physical bonds can develop. The few experiments that have been performed show that the forces of adhesion in general increase with decreasing particle size and with increasing time of surface contact" [4].

Having been drawn toward an interface by gravitation or swept toward it by convective currents, wind action, or other "mechanical" means, potential soilants may be more closely attracted by "long-range" forces, then attached by physisorption and chemisorption. Detailed discussions may be found in many books, including the classic treatise of Adamson [9] and a briefer, but excellent, text by Myers [10].

Long-range forces comprise electrostatic interactions, which are as powerful as covalent bonds and decay with the inverse square of the distance between charges, and van der Waals forces. Van der Waals forces can be further subdivided into permanent dipole-permanent dipole interactions (two orders of magnitude less powerful than covalent or electrostatic bonds and responsive to the inverse cube of the interdipole distance); permanent dipole-induced dipole interactions, with energies proportional to the inverse sixth power of the interpolar distances; and London dispersion forces, also proportional to the inverse sixth power of the distance. Dispersion forces, the most important to adhesion, arise from quantum mechanical effects, are exerted by all chemical species, and can act over ranges as long as 10 nm [9,10].

Once long-range forces bring a sorbent and substrate together, the stage is set for physisorption and chemisorption. Figure 5 reproduces a diagram of the overlapping regions of these phenomena, demonstrating that they must be cooperative. "Curve 1 represents the energy diagram for physical adsorption. . . As the [sorbent] approaches the surface, there develop van der Waals interactions leading to an energy minimum representing the heat of adsorption, ΔH_{ads}. At some distance, there begins to develop . . . a repulsive interaction. Curve 2 represents . . . chemisorption, which . . . involves specific interactions between the adsorbent and the adsorbate. . . If the two adsorption processes were mutually exclusive, the activation energy of chemisorption [ΔH_{chem}] would be so high that it would occur only under rather vigorous conditions. . . . it becomes clear that physical adsorption is an important component of the overall chemisorption" [11].

Chemisorption is "by nature limited to the formation of a monomolecular adsorbed layer, . . . whereas physical adsorption has no activation energy, . . . is diffusion controlled, [and can] form multimolecular thicknesses in a pseudo-liquid assembly (as in the B layer of Fig. 4) [12]. Chemisorption is relatively slow because of an activation energy barrier, operates only within the range of chemical bond distances, and can be regarded as playing no role in the <u>initial</u> attachment of soilants" (present author's underlining).

3. The Unique Aspects of Aerosol Impingement and Adhesion

Aerosol impingement is of great concern for solar energy applications, particularly in seashore regions where atmospheres laden with salt and pollutant aerosols are common. Liquid or solid aerosols impinging on and adhering to surfaces constitute very special cases of liquid/solid and solid/solid interactions. Particles descending to one µm or below are of the same order of magnitude as surface roughness, making it possible for actual embedment to enhance the more usual forces leading to adhesion. Small aerosol diameters, their potentials for labile electrostatic charging, and their extensive dispersion greatly enhance adhesion in a complicated manner.

To quote Rumpf and Schubert: "This is the world of fine particles; <u>their behavior depends much more on surface phenomena than on volume forces</u>" (present author's underlining) [13]. Adhesion to a substrate of particles larger than one cm in diameter is very sensitive to gravitational effects. As particle size diminishes, gravitational influences decrease rapidly, but adhesional influences such as material bridging, sintering, van der Waals attractions, and electrostatic effects (see Fig. 6) remain powerful. As Myers observed, "It is recognized that the main driving force for sintering is surface tension rather than external pressure. Atoms or molecules located at sharp asperities on the surface experience a greater surface tension force and have a greater surface mobility than those on planar surfaces. Furthermore, the actual area of contact between particles undergoing sintering will be small so that even at relatively low total pressures, the pressure applied at the points of contact will be multiplied so as to exceed the yield value of the material" [15].

Davies, in a classic 1973 review of experimental literature on particle adhesion, filter clogging, and filter penetration [16], concluded that:

- The probability of liquid or solid particle adhesion depends directly on aerodynamic drag and therefore on both velocity and particle size.
- Adhesion begins to fail at a flow rate of 4 m/s for particles greater in diameter than 0.5 μm. At flow rates below 1 m/s, adhesion is nearly complete for all particles up to 1 μm in diameter. Initial deposition efficiency and adhesion decrease with increasing collision velocity.
- Deposited particles are rarely distributed evenly over surfaces and often build up chain aggregates [at asperities] to form pseudo-fibrils (Fig. 7).
- Particles with diameters of 2 to 6 μm are very unlikely to be redispersed after adhesion to reasonably clean surfaces.

Consistent with this, Roth and Pettit's particle-size distribution measurements showed that small particles are preferentially retained at mirror surfaces. Moreover, particles within the aerosol range produced the most catastrophic effects on mirror reflectivities [4].

4. Relationship of Soiling Propensity and Surface Energy

A-layer soiling is a powerful expression of the universal drive toward the lowest free-energy states. An array of molecules in the asymmetric surface environment is virtually defined by its high energy, relative to that of an array of the same type and number of molecules in the bulk. "Excess" (surface) free energy arises from the unique interfacial environment, in which atoms experience the effects of anisotropic force fields. The manner of surface preparation and postpreparation history greatly influence surface energy; a rough surface, for example, will have tightly focused high-energy regions surrounding asperities. Frictional wear and corrosion, as well as adsorption, can radically modify surface energy.

Metals have intrinsically high surface energies, and " 'clean' surfaces of . . . crystalline, metallic, and inorganic glassy materials, (with) surface energies of 10^2-10^3 mJ m^{-2}, . . . will literally "do anything" in order to lower their surface energies, including especially the adsorption of almost any available molecule . . . nitrogen, oxygen, water, or any other material present in the environment" [17]. The kinetics of such adsorption are extremely rapid at high-energy interfaces and much slower at the surfaces of polymers, which are generally characterized by lower surface energies, polydispersity, noncrystallinity, and randomness. Polymers, however, experience virtually constant chain relaxations in their continuous attempts to approach equilibrium, with slow but real effects on surface energies and sorptive propensity. Adsorption at the surface of glass is intermediate in rate between metals and polymers.

Water, present to some extent in even desert atmospheres, exerts a particularly important influence: "Even very hydrophobic, rigid polymers such as polymethylmethacrylate which contains somewhat hydrophilic ester side chains will, in contact with water, undergo surface molecular reorientation due to the interaction of water with the ester groups. The interfacial region becomes plasticized (roughly put, softened) because the water-ester interaction liberates to some extent the side chains and increases their mobility . . . these surface interactions can dramatically change the interfacial characteristics of a polymer. . . .Glass (as well). . . has been shown to undergo interactions with liquids such as water which lead to specific alterations in its surface properties" [18].

5. Experimentally Relating Surface Energy and Wettability to Adhesion

Direct determinations of surface energy are impossible for solids because, by definition, they cannot be reversibly deformed; expansion or contraction introduces bulk strains that energetically dwarf surface free energy. Adhesiveness and its antithesis, abhesiveness, thus can be related to surface energy through wettability, an experimentally accessible measure of the density and uniformity of interfacial contacts [19].

During wetting, an interface between the substrate surface and one fluid (air or test-liquid-saturated air) is replaced by an interface between the same substrate and a second fluid (the test liquid). Both the thermodynamics and the kinetics of this process are multifaceted, and the kinetics have not been amenable to treatment by hydrodynamic theory. Thus, the reality is emphasized that wetting and sorption are functions not only of the properties of the substrate, the incumbent fluid, and the displacing fluid, but also of the two substrate-fluid interfaces and the single fluid-fluid interface.

Predicting adhesiveness from wettability starts with Young's equation describing the shape (contact angle) of a liquid drop on a solid. Zisman defined an empirical "critical surface tension" or CST (a) for solids, based on the extents to which they could be wetted by liquids of different surface tensions [20]. Ogarev [21] combined the defining equation for work of adhesion (W_{SL}) and the Girifalco-Good equation [22] as condensed by Huntsberger [19] with the mathematical expression of the Zisman CST, then differentiated to obtain

$$W_{SL,\ \mathrm{maximum}} = 0.04\ [1 + 0.04(\mathrm{CST})]^{2})/2 \quad .$$

Thus, the CST of a solid is a justifiable indicator of its work of adhesion. In general, it is understood that a necessary, but not sufficient, condition for liquid adhesion is that the surface tension of a spreading liquid must be lower than the CST of the substrate [23]. One characteristic of an adhesive surface will be a low CST.

We often describe a surface in terms of its hydrophilicity (oleophobicity) or oleophilicity (hydrophobicity), implying a wettability spectrum like that shown in Fig. 9, which shows the influences of both chemistry and morphology on CST (labeled in this chart as γ_C). This wettability spectrum covers the range of possible dispersion-force interactions, which are markedly reduced when either a surface or an adherend is perfluorinated. Most materials are fluorophobic, and perfluorinated materials are both hydrophobic and oleophobic, indicating that fluorination is an excellent approach to imparting adhesiveness. Moreover, configuration of a surface in either an oriented-monolayer or a crystalline morphology is likely to enhance adhesiveness.

III. SURFACE-MODIFICATION TECHNOLOGIES

As long ago as 1967, a Symposium on Interface Conversion for Polymer Coatings emphasized rendering metallic or nonmetallic substrates more amenable to the attachment of polymer coatings [24]. Recognition of the critical importance to many technologies of interfaces and, therefore, of interface modification, has blossomed over the last decade. There are now regular meetings of the International Conference on Surface Modification Technology, which focuses chiefly on alterations of metallic and ceramic interfaces, and Gorham Advanced Materials Institute very recently organized "Thin Films '91," its third "international business and technical conference focusing on the growth of the $10 billion thin films market in the 1990's" [25]. Several journals, notably the Journal of Adhesion Technology and Thin Solid Films, regularly publish related articles.

Techniques for characterizing interfaces have burgeoned in recent years, spurring both increased appreciation of the meaning of cleanliness and the development of new methods for approaching it. These analytical approaches (including Auger electron spectroscopy [AES], X-ray photoelectron spectroscopy [XPS], electron spectroscopy for chemical analysis [ESCA], ion scattering spectroscopy [ISS], secondary ion mass spectrometry [SIMS], ellipsometry, plasma chromatography, ion chromatography, microfluorescence, evaporative rate analysis, indium adhesion, surface potential difference, wettability, scanning tunneling microscopy [STM], atomic force microscopy [AFM], and many others) reach a precision and resolution undreamed of only a few years ago.

Surface cleaning and modification technologies are legion and include, but certainly are not limited to, treatments with solvents, plasma, ultraviolet (UV)/ozone, mechanical ablation, ion milling, ion implantation, laser ablation, chemical vapor deposition (CVD), plasma-assisted CVD, ion beam deposition and etching, sol-gel or polymer coating, photo-induced reaction, cathodic sputtering, surface chemical attack, and various hybrid technologies. Many, if not most, of these are more suitable for modification of ceramics or metals than for modification of polymers [25].

Any acceptable soiling-prevention technology must exert either beneficial or minimal negative effects on such original material characteristics as rigidity, density, and coefficient of thermal expansion. If a modification does not enhance stability toward physical, chemical, and thermal degradation, it must, at the very least, not destabilize. Solar energy applications place one very special demand on interfaces: any coating as thick or thicker than one-quarter of the wavelength of visible light is likely to disturb the optical characteristics that are of primary importance. Thus, a modified interface either must have precisely the same set of optical properties, including refractive index, as the original surface, or it must be thinner than 120 nm. It stands to reason that a coating with optical properties identical to those of the bulk is likely to be compositionally identical and, thus, similarly adhesive. The preferred modification, therefore, will produce an extraordinarily thin adhesive coating that is molecularly smooth and permanent.

Among surface treatments directed specifically at improving the performances of solar energy and optical devices have been antireflection coatings through sol-gel processing of optical thin films [27], fabrication of polycrystalline thin films for photovoltaic devices [28], coating of photovoltaic devices with a fluorinated silane that bonds covalently with the surface [29], and plasma polymerization of fluorinated monomers at the interface [30]. Implantation of fluorine at the surface might appear to have great promise for increasing adhesive and barrier characteristics of polymers; there are indications, however, that the damage incurred by polymer exposure to an ion beam actually overwhelms any barrier properties that might result from fluorine addition [31].

IV. ULTRATHIN ORIENTED MOLECULAR FILMS FOR SOIL RESISTANCE: ANTI-FOULING TECHNOLOGY (AFT)

It is clear that intervention before long-range substrate and adherend forces can swing into operation will prevent the physisorption and chemisorption necessary to soiling. The most direct and practical approach will minimize asperities and cancel or reduce the London dispersion forces exerted by the substrate in the direction of potential adherents.

A. Oriented Molecular Films for Soiling Resistance

Compositionally, oriented films are formed from amphophilic compounds; their unique behavior results from the high precision with which they can be packed and oriented on a surface, as well as their thinness (~ 25 Å) and the tenacity with which the first monolayers often cling. For many years after their discovery by Langmuir [32] and initial explorations of their properties by Blodgett [33], oriented films were regarded exclusively as laboratory toys. As two recent books on the subject [34,35], many reports in the scientific journals, and Chapter 17 in this volume attest, however, fundamental and applied research in the area has been vigorous over the last decade; it is probable that industrial applications are just around the corner.

Monolayer films can be applied to a variety of substrates, including polymers, glass, and ceramics, either by the classical Langmuir-Blodgett (LB) dipping technique (LB films) or by the formation of self-assembled monolayers (SAM). Both technologies, as well as properties of the films and many potential applications (but not antifouling) are described in detail in the books referenced. Substrates covered with intact oriented films often display a combination of properties directly opposite to those known to potentiate soiling or fouling: they are physically smooth on a molecular scale, usually hydrophobic, and chemically homogeneous.

Figure 10 schematically represents the heliostat surface of Fig. 1, now "ideally" coated with an oriented monomolecular film of a long-chain pyridinium bromide (R_fPyrBr), and where R_f represents a hydrocarbon chain fluorinated at one end. It is apparent that the heliostat surface has been radically altered with regard to those properties that potentiate soiling: molecular smoothness has been conferred by the LB film, the static charge has been at least partially neutralized, and impinging soil particles may now be repelled by the perfectly oriented low-energy perfluorinated methyl layer. This approach to converting a surface from attractiveness to repulsiveness toward soilants has been given the acronym AFT, for Anti-Fouling Technology [36].

B. AFT for Membrane Separations

The utility of AFT was first explored for anion-exchange membranes in electrodialysis (ED) stacks. These membrane systems are most seriously affected by fouling; because of their negative charges, most foulants are electrostatically attracted to the permanent positive charges on the membranes. The resulting fouling leads to sharp increases in the power requirements for the stacks and severely limits the application of ED.

In a 1981 research effort supported by the Department of the Interior, my coworker and I deposited LB films on two types of commercial polymer anion-exchange membranes, challenging the resulting "composites" in a laboratory ED stack for up to 184 h by concentrations of (sodium humate) foulant four orders of magnitude greater than those occurring in natural waters [37,38,39]. The electrical resistance of a stack containing untreated membranes is profiled in the central curve of Fig. 11. Only one oriented molecular layer of a fluorinated amphophilic material on the membrane effectively prevented increases in resistance (the lowest curve of Fig. 11), indicating enhanced adhesiveness at the membrane surface.

Conversely, a single molecular layer of arachidic acid significantly increased the initially observed electrical resistance, as well as potentiating rapid rise to a steady-state resistance almost twice that of the untreated membranes (top curve of Fig. 11). The initial high resistance presumably was due to formation of a high-resistance "sandwich" membrane by the LB film of neutral or negatively charged foulant (arachidic acid) at the surface of the positively charged membrane. This nonfluorinated oriented layer (a perfect "A" layer) may then have served as a base for denser attachment of B and C layers than ordinarily could have occurred. The influences of AFT on wettabilities of these membranes correlated well with their soiling resistances. The rate at which untreated membranes sorbed (with swelling) a standard water droplet was noticeably retarded by treatment with fluorinated films and enhanced by layering with arachidic acid.

Later work showed AFT to be effective as well for pressure-driven membrane separations, in which the usual figure of merit is flux at constant pressure. Figure 12 shows the effect of fluorinated LB films on the fluxes of polysulfone ultrafiltration membranes during the first 7 hours of operation under dead-end fouling conditions [40,41]. At first, the flux of both treated membranes is lower than that of the control being stirred at the same speed, indicating that the LB film has reduced the pore sizes; within only 3 to 4 h, however, there is crossover because of the rapid flux decay of the untreated control.

Figure 13 summarizes the results, between 10 and 23 h after initiation, of humate fouling experiments with regenerated cellulose ultrafiltration membranes under a different set of ultrafiltration conditions [42]. Total permeate volume is the consequence of cumulative flux; concentration of foulant at the membrane surface reflects both membrane selectivity and the challenge against which the membrane must work. Treatments with FHxUA (perfluorohexyl undecanoic acid) and FHpPB (perfluoroheptyl undecanyl pyridinium bromide) produced highly efficient composites that were more selective while simultaneously maintaining higher fluxes, even against both precipitated gels of humate and the highest possible solution concentrations of humate.

C. AFT for Heliostats

In 1985, my research group at Georgia Institute of Technology undertook two successive SERI-sponsored programs to determine whether AFT might provide effective soiling protection to heliostats while maintaining the original optical properties. Although there were significant problems with reproducible deposition of LB films due to the hand-operated equipment and poor vibration isolation, the results indicate that AFT may be an important step toward adhesion enhancement, especially in devices for which thinness and precise arrangement of the modifying layer are critical [43].

The substrate of choice was ECP-300A, a four-layer film (polyester release liner, acrylic adhesive, silver reflecting layer, polymethylmethacrylate coating) fabricated by the 3M Company, Energy Control Products Division, for glass- or aluminum-supported or stretched-membrane heliostats. As received, ECP-300A did not readily accept LB layers, possibly because of contaminants or because manufacturing additives like UV retardants had become segregated at the surfaces; brief oxygen plasma treatments prior to layering resolved this problem.

We developed a "mud-pack test" for initial screening, coating heliostat samples with a thick slurry of common Georgia red clay in tap water. After drying horizontally for 24 h, the samples were rinsed for about 1.5 min under running tap water and allowed to dry again before their reflectivities were measured by FTIR (Fourier transform infrared) spectroscopy. This challenge "exaggerate[d] the [adhesive] difference[s] between different coatings" [43]; treatments that survived it were used to prepare samples for SERI.

In tests more readily extrapolatable to real-life exposure, Pitts of SERI dusted the samples with standard dust from an air-driven gun and exposed them in an accelerated weathering tester for two light cycles followed by condensing humidity [44]. This exposure cycle is said to be equivalent to 1 year of outdoor exposure. After samples had air dried for 1 to 2 h and been rinsed with deionized water from a paint sprayer, their relectances at 650 nm were measured at four different full-cone angles of 4, 8, 12, and 31 mrad at SERI.

As cost matching for an earlier government contract [39], 3M had provided to us a variety of proprietary fluorinated surfactants, which were re-examined for this application. Two of these, 3M compound L-10089 (a fluorinated carboxylic acid) and 7F10H itaconate (7F10HItc, perfluoroheptyl undecanyl itaconate, a polymerizable fluorinated amphiphile), showed promise.

Figures 14 through 16 compare representative reflectance spectra of the best (most reflecting) samples of untreated heliostat controls with the best treated samples of each type after one mud-pack challenge followed by rinsing. Post-mud-pack reflectivities are summarized in Fig. 17. Reflectivities of ECP-300A coated with one monolayer of 7F10HIt, L-10089, L-11238, and L-11239 were significantly higher than that of the control after one challenge cycle, while three layers of 7F10HIt appeared to confer approximately the same protection as one layer of the same compound. One particular treatment with carboxylic acid L-10089 provided protection far superior to that of any other, including coating with three layers of the same compound. In view of the mechanical problems with film deposition, we believe that this sample (Fig. 16, 33f) provides an example of the performance that may be expected when the LB coating has been applied with the greatest possible control of order, orientation, deposition speed, and other process parameters.

Figure 18 shows that, in several but not all cases, average contact angles of pure water on ECP-300A were increased by monolayers of fluorinated materials. Compound L-1028 was a fluorinated quaternary ammonium salt, and L-11238 and L-11239 were both fluorinated acrylates that were polymerized after deposition. The three films that produced reflectivity increases as monolayers had the same effect when deposited in trilayers. Reflectivity results cannot be strictly correlated with the wettabilities: the effect of L-10089 on water contact angle was by no means dramatic, although one sample was strikingly nonwettable. Moreover, wettability was apparently decreased by a polymerized monolayer of fluorinated acrylate L-11239, even though this compound afforded some protection against soiling (Fig. 17).

Figures 19 and 20 profile representative SERI reflectivity evaluations at 4 mrad as samples were subjected to 20 soiling-cleaning cycles. Results of the SERI tests at all cone angles are summarized in Figure 21, where it is evident that a 4-mrad cone angle exposes reflectivity differences most effectively. Samples 29 and 31 had been treated with one and three layers, respectively, of 7F10HITc, and samples 33 and 35 were treated with one and three layers, respectively, of L-10089. All treated samples showed higher reflectivities than untreated controls at virtually every stage of the test, with highest honors reserved for a sample coated with one layer of L-10089 (Figure 20). As Shutt noted, "the effect of the AFT coating did not diminish in time, indicating that the film is sufficiently robust to endure extreme environmental exposures. . . . since the sample showed no apparent decreasing trend in time, it is believed that the protection which is afforded by the AFT coating would last substantially longer than this in actual use" [43].

Finally, Fig. 22 compares post-mud pack photographs of an L-10089-treated sample of ECP-300A(a) and an untreated control sample (b). Photograph a, on the left, is mostly dark because it images the camera pointed toward the sample, i.e., its surface reflectivity has survived the challenge of the dried soil. In contrast, the control was encrusted with soil except where it had been mechanically wiped, and it demonstrates virtually zero reflectivity.

V. CONCLUSIONS AND RECOMMENDATIONS

On the bases of both theoretical considerations and the exploratory studies reported above, AFT may well be a viable solution to the soiling-related problems of solar technologies. The influence of the fluorinated LB film on wettability and permeability may positively benefit delamination tendencies and corrosion of the silver layer. AFT also could impart abrasion and wear resistance, as has been well demonstrated by a recent flurry of research on the tribology of oriented films [34,35].

Much work remains. There has not yet been adequate exploration, under optimized conditions, of the relative influences of the substrate-oriented film interaction, amphiphile chain lengths, the nature of permanent charges, degrees of ionization, extents of fluorination, the density of amphophilic chain packing, and other relevant parameters. We have observed, for example, that improved ordering of a substrate surface produces higher quality and presumably more permanent LB films. There are now a number of polymerizable fluorinated amphiphiles, one of which may lead to significant improvements in durability. Lifetime testing on a statistically valid number of samples is an essential task. Finally, once optimal systems have been decided on, it will be necessary to establish the methods and best processing windows for production of antisoiling coatings.

VI. ACKNOWLEDGMENTS

Mr. Walter Forrister and Dr. Daniel P. Campbell were vital members of the AFT-heliostat research team during the 2 years that I directed it, making many valuable contributions. Dr. Joel D. Shutt succeeded me as project director and prepared the Final Report; his scientific integrity and communication skills are greatly appreciated. I wish to thank the Research Library staff of the Eastman Kodak Company, particularly Ms. Diane Ely, for their timely assembling of the literature reviewed for this paper.

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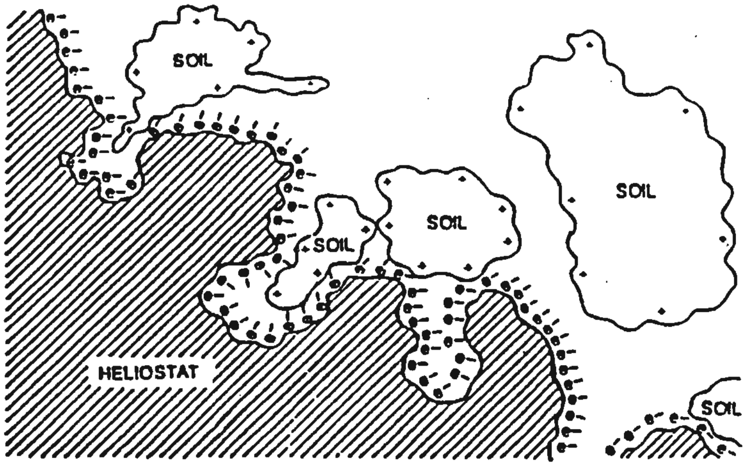

Figure 1. Heliostat soiling from a molecular point of view

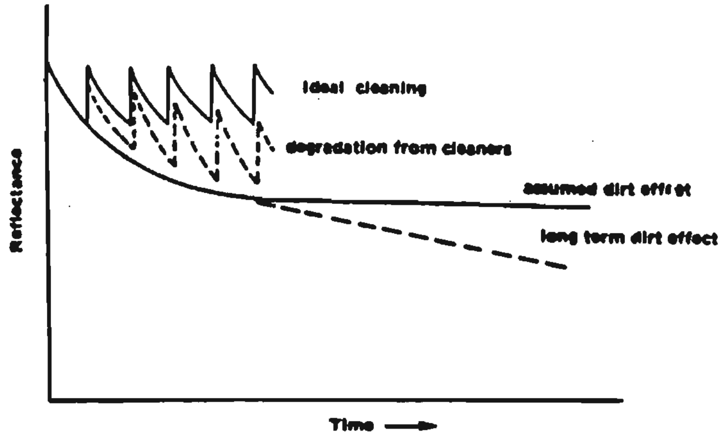

Figure 2. Expected long-term reflectance behavior of an exposed mirror, with and without periodic cleaning (from Reference 4)

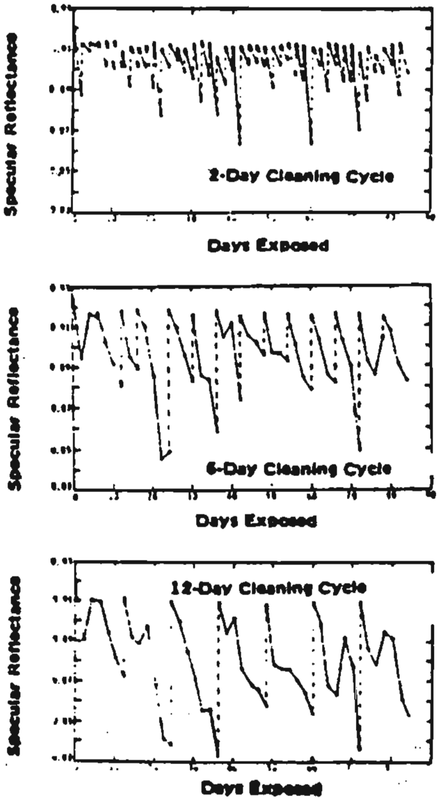

Figure 3. Specular reflectance of mirrors undergoing (a) 2-day, (b) 6-day, and (c) 12-day cleaning cycles. The solid lines trace losses as the mirrors soil, and the dashed lines trace reflectance restored on cleaning (from Reference 4).

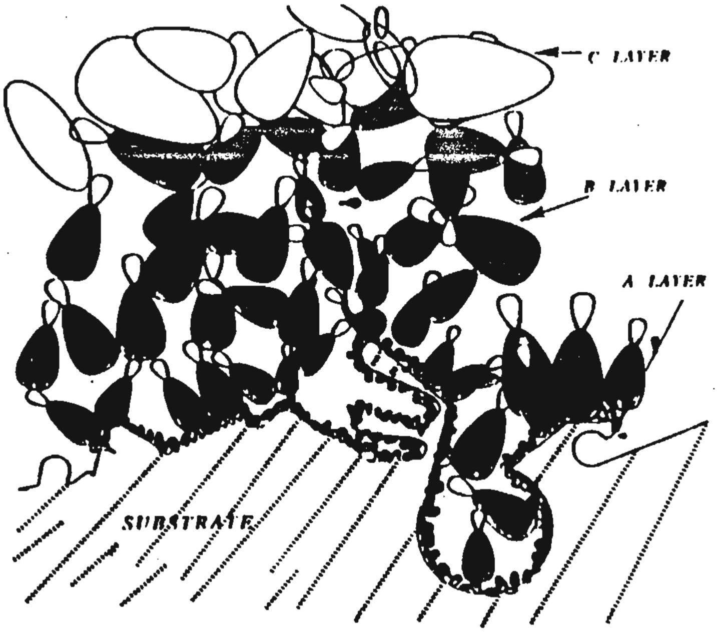

Figure 4. Eirich's and Patrick's "Hierarchy of Spontaneously Adsorbed Layers"

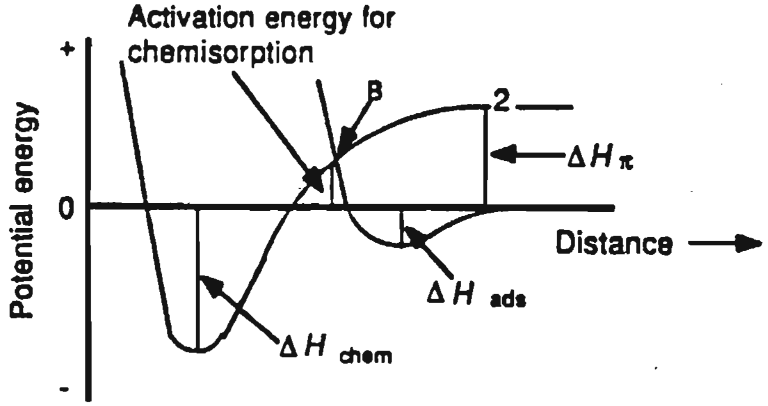

Figure 5. Schematic of energetic paths of physical adsorption and chemisorption, showing the crossover point at which they become cooperative phenomena (from Reference 10)

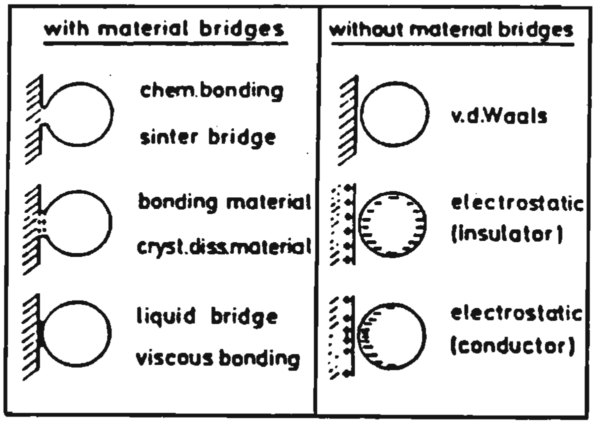

Figure 6. Various mechanisms by which aerosol particles irreversibly adhere to surfaces, including material bridges (from Reference 14)

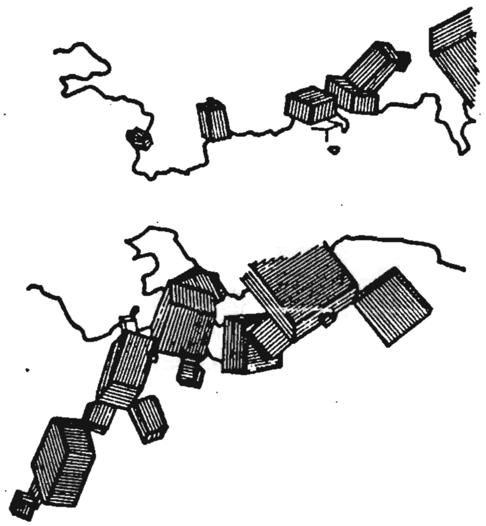

Figure 7. Buildup of localized chains in preference to homogenous distribution of sodium chloride aerosol (Watson, as cited in Reference 16)

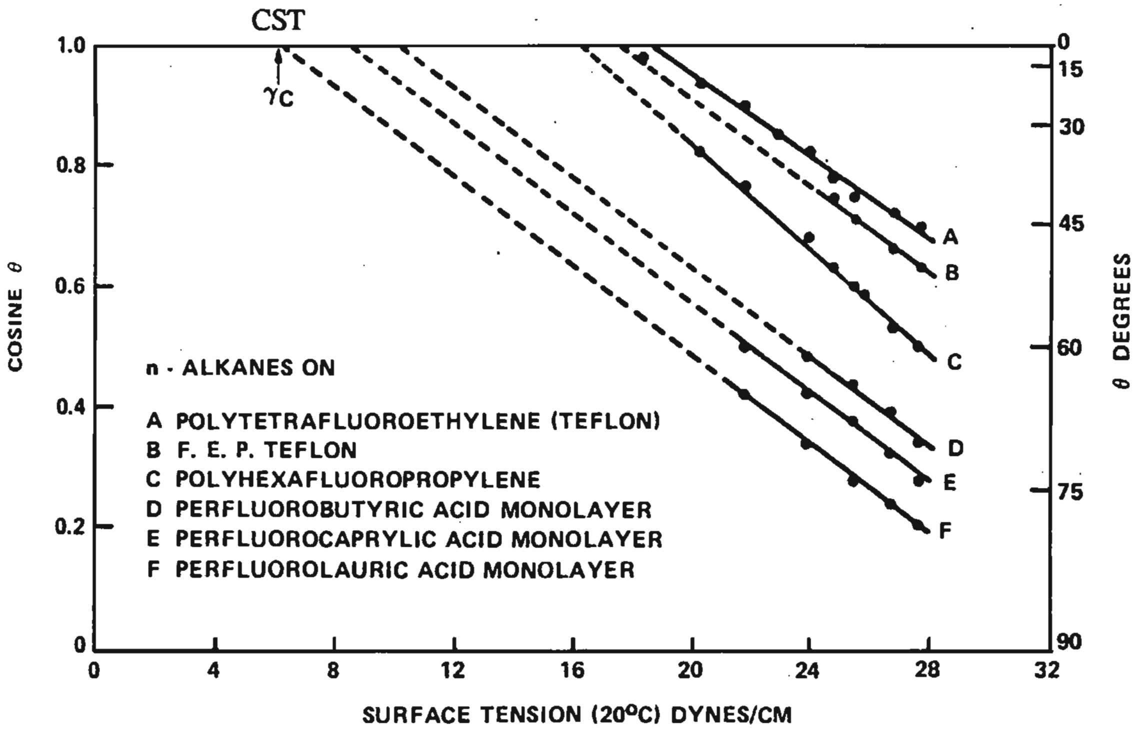

Figure 8. Contact angles for a series of liquid n-alkanes on fluorinated solid surfaces. The intercepts (CSTs or γ_Cs) represent the "critical surface tensions" of the solids (from Reference 20).

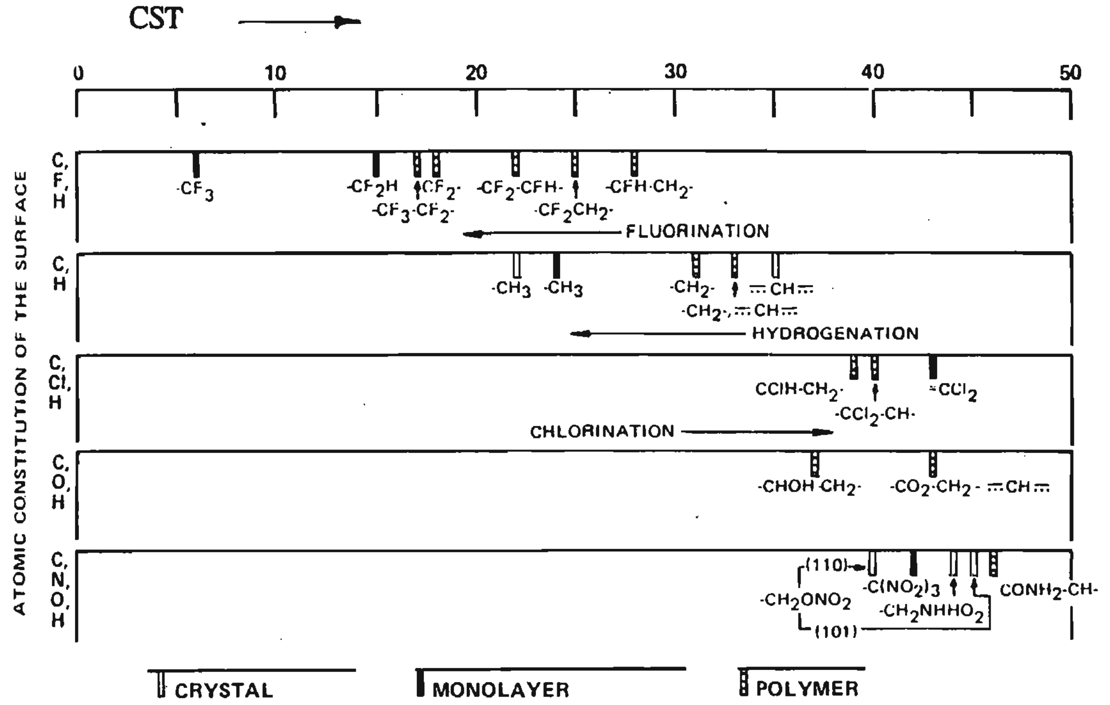

Figure 9. The wettability spectra of selected low-energy surfaces, showing effects of chemical and morphological modifications (from Reference 20)

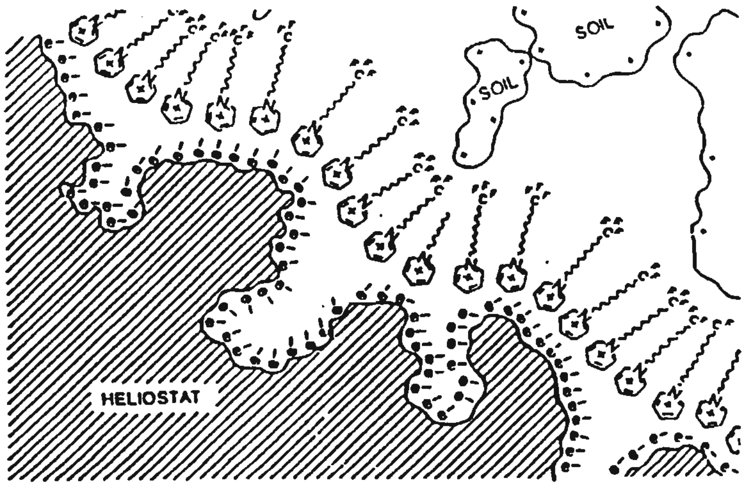

Figure 10. Schematic of heliostat surface protected from soiling by an ultrathin oriented monomolecular film

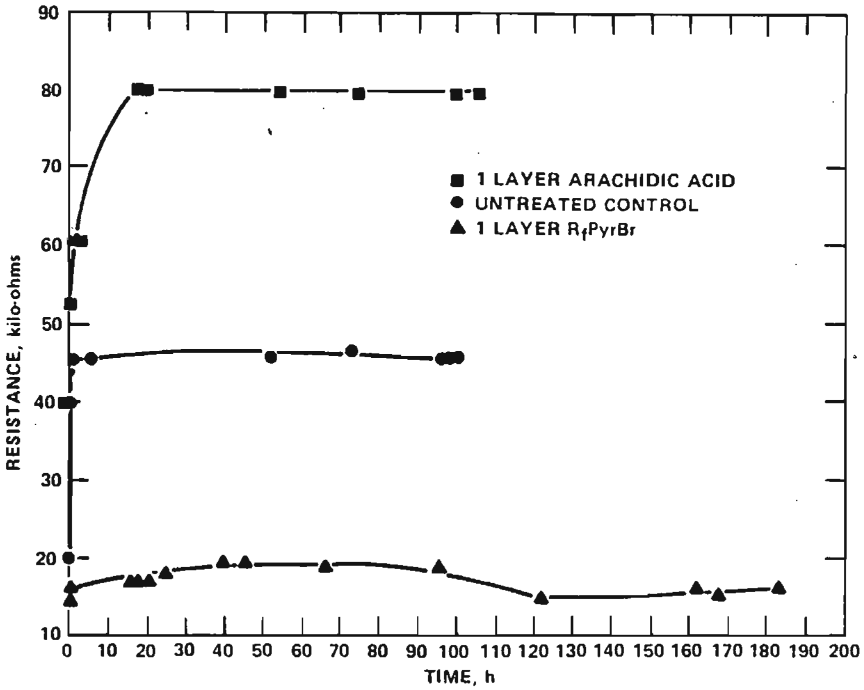

Figure 11. Electrical resistance profiles of electrodialysis cells containing aqueous sodium humate challenges of untreated anion-exchange membranes (central curve), membranes treated with one LB layer of arachidic acid (top curve), and membranes treated with one LB layer of a fluorinated amphiphile (from Reference 37)

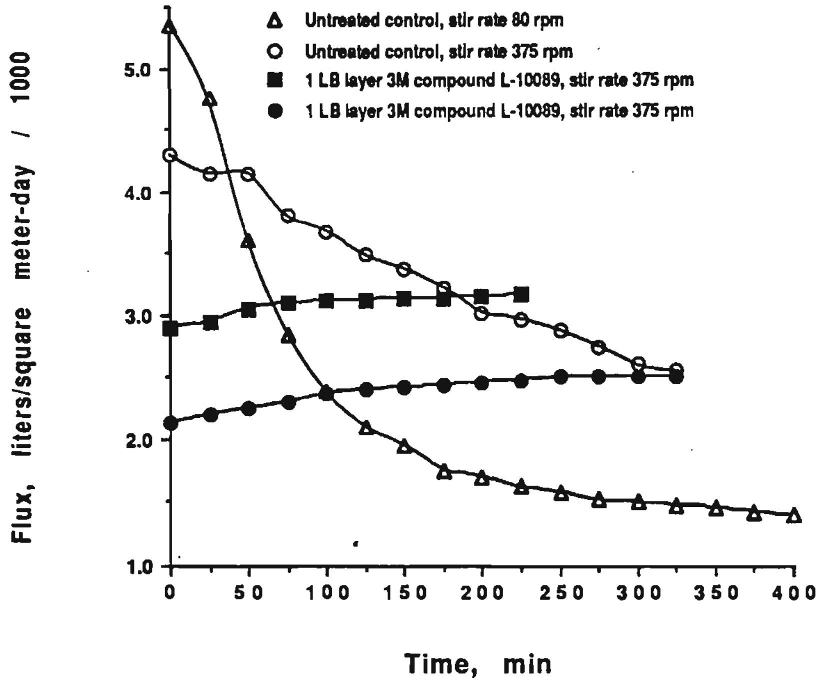

Figure 12. Flux profiles of polysulfone membranes challenged at 40 psig in a stirred dead-end ultrafiltration cell by 25 ppm (initial concentration) sodium humate solution (from Reference 40)

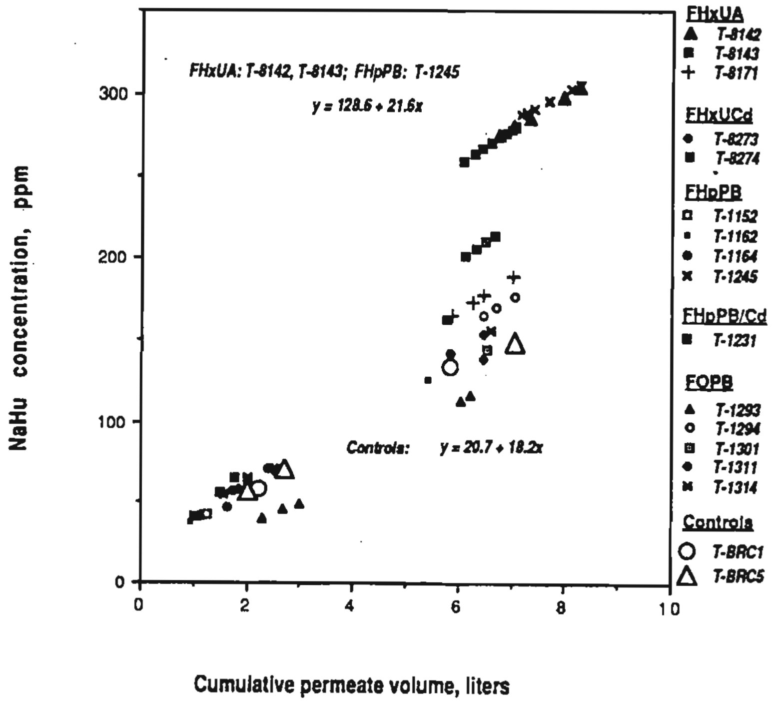

Figure 13. Nominal concentrations of sodium humate in retentate as functions of total permeate volumes for two control membranes (BRC-1 and BRC-5) and membranes modified by LB monolayers to various fluorinated amphiphiles. Tests were run at 25 psig in stirred dead-end ultrafiltration cells against initial concentrations of 25 ppm humate (from Reference 42).

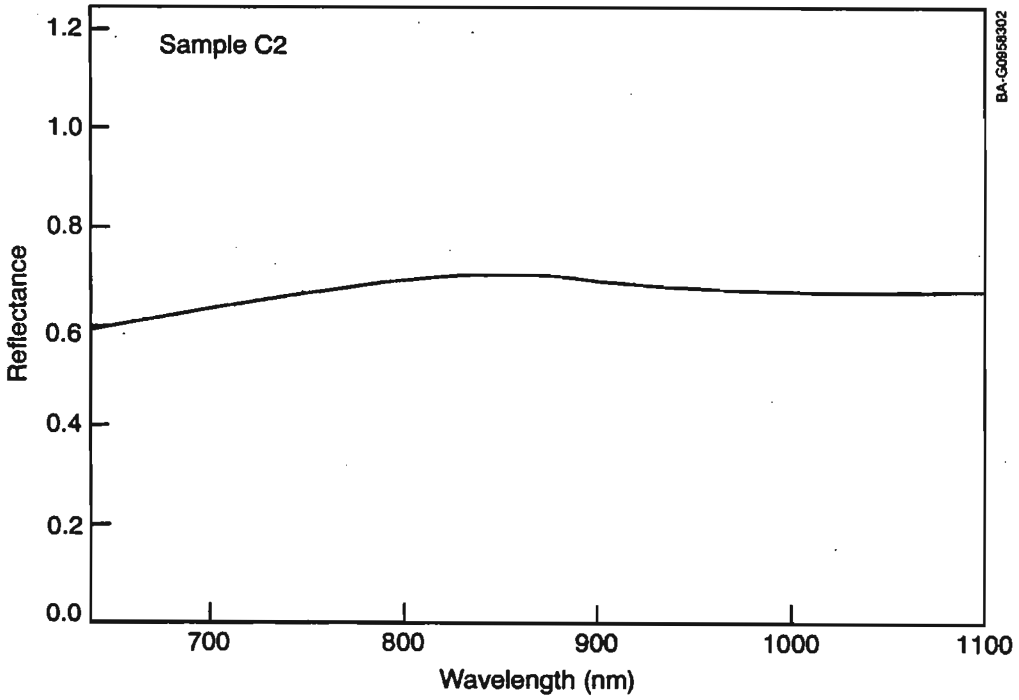

Figure 14. "Residual" FTIR reflectance spectrum of untreated control ECP-300A, after mud-pack challenge and rinsing (from Reference 43)

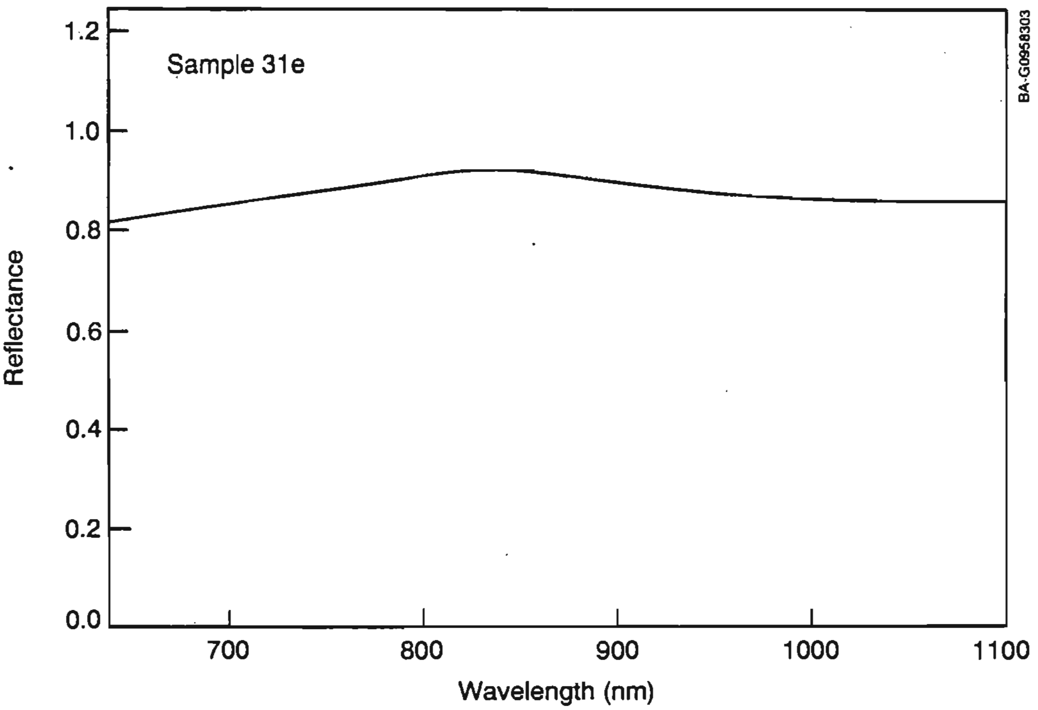

Figure 15. "Residual" FTIR reflectance spectrum of ECP-300A treated with one oriented layer of 7F-10H itaconate, after mud-pack challenge and rinsing (from Reference 43)

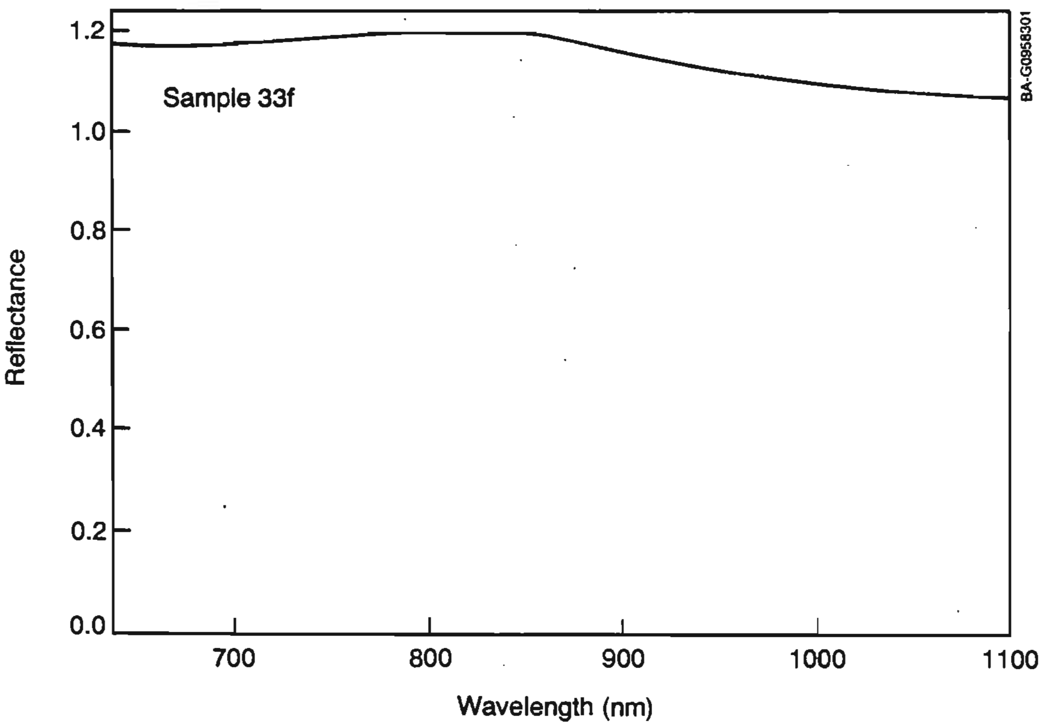

Figure 16. "Residual" FTIR reflectance spectrum of ECP-300A treated with one oriented layer of 3M compound L-10089, after mud-pack challenge and rinsing (from Reference 43)

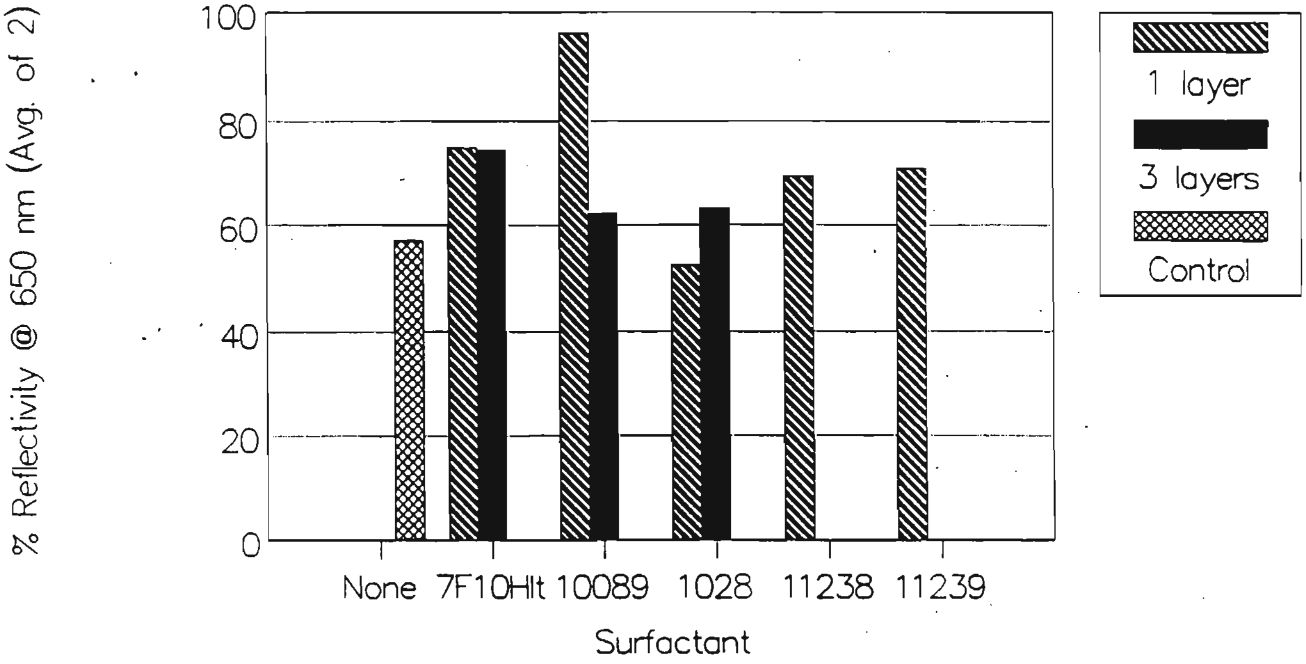

Figure 17. Summary chart of "residual" FTIR reflectivities at 650 nm, after mud-pack challenge and rinsing, for ECP-300A treated with LB films of fluorinated amphiphiles (from Reference 43)

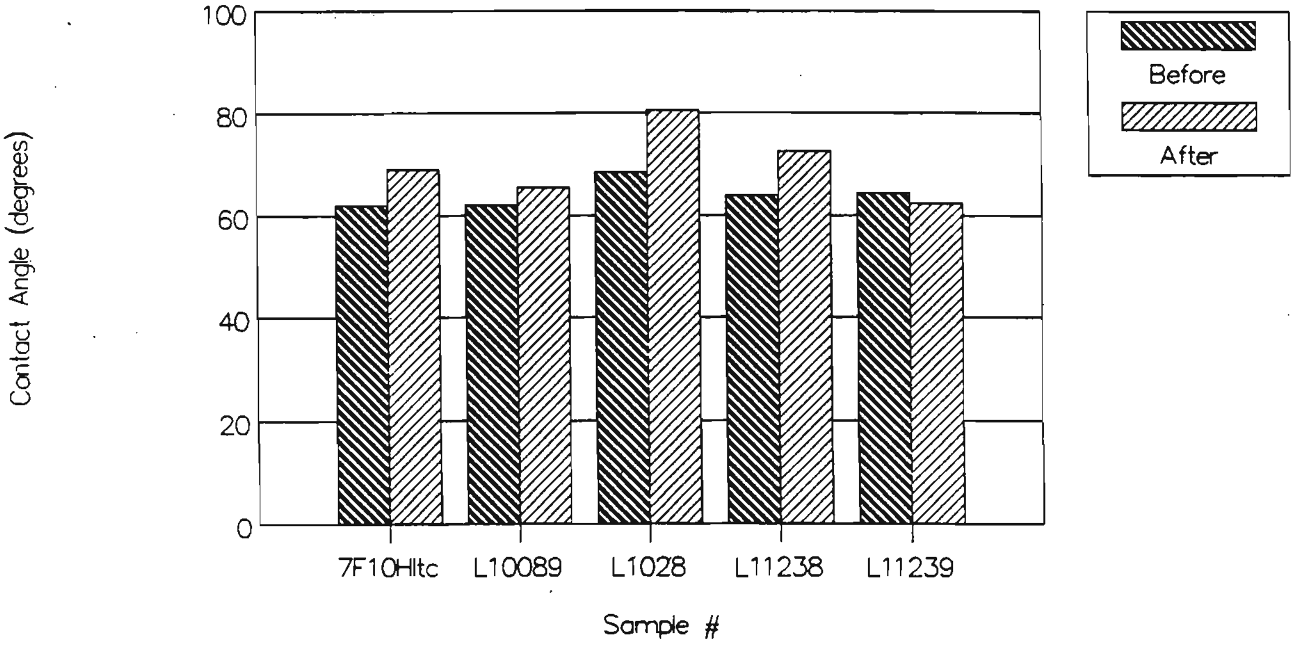

Figure 18. Effect on ECP-300A-water contact angles of coating with single oriented layers of various fluorinated amphiphiles. The compounds are briefly described in the text (from Reference 43)

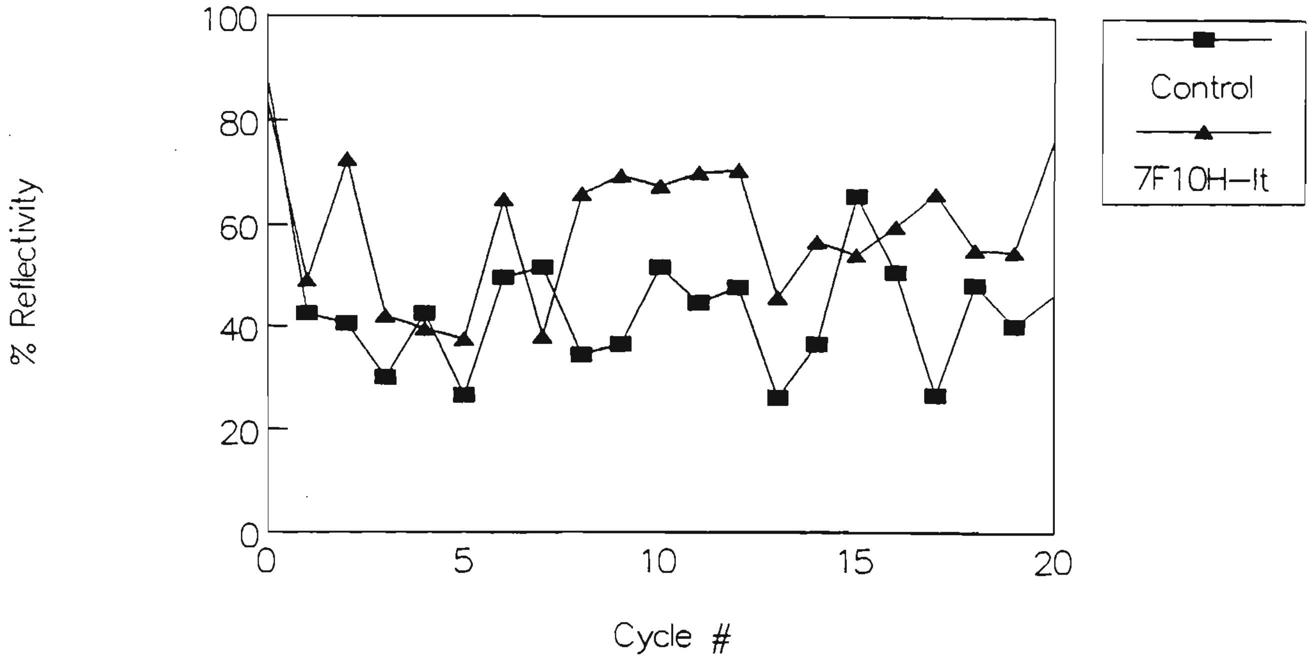

Figure 19. Effect of soiling and cleaning by 20 cycles of the SERI protocol (described in the text) on the reflectivity of ECP-300A treated with one LB layer of 7F10H-itaconate (from Reference 43)

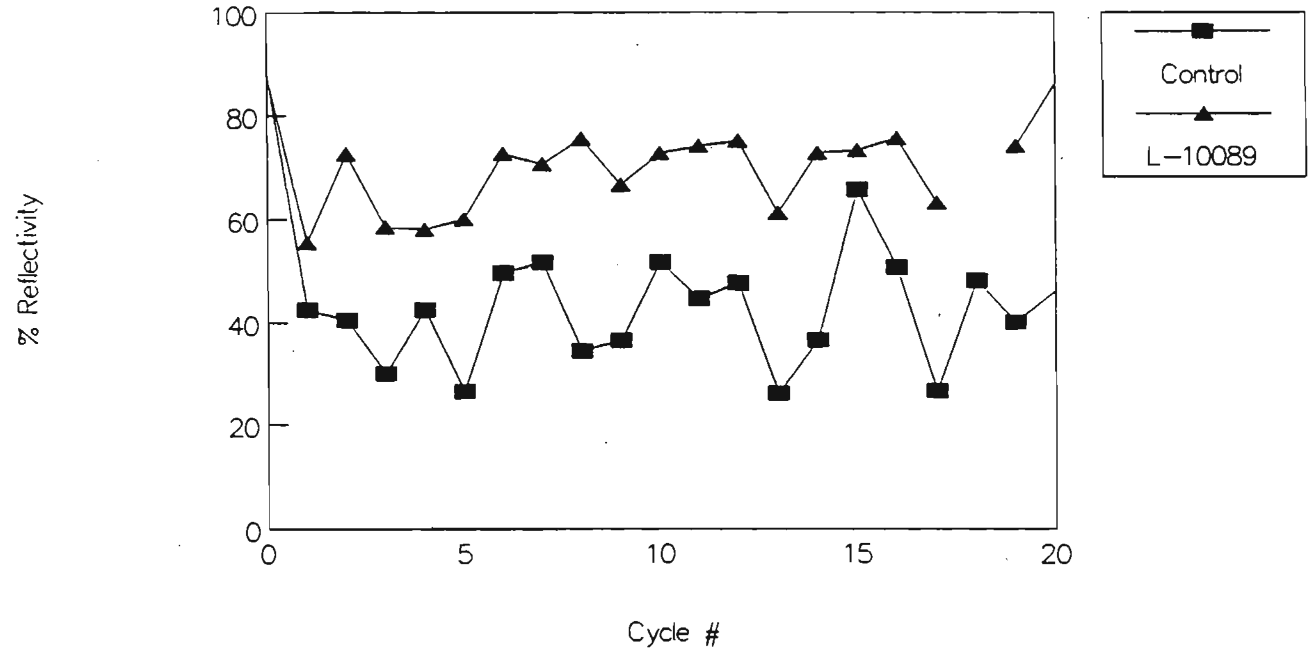

Figure 20. Effect of 20 cycles of soiling and cleaning by the SERI protocol (described in the text) on the reflectivity of ECP-300A treated with one LB layer of 3M compound L-10089 (from Reference 43)

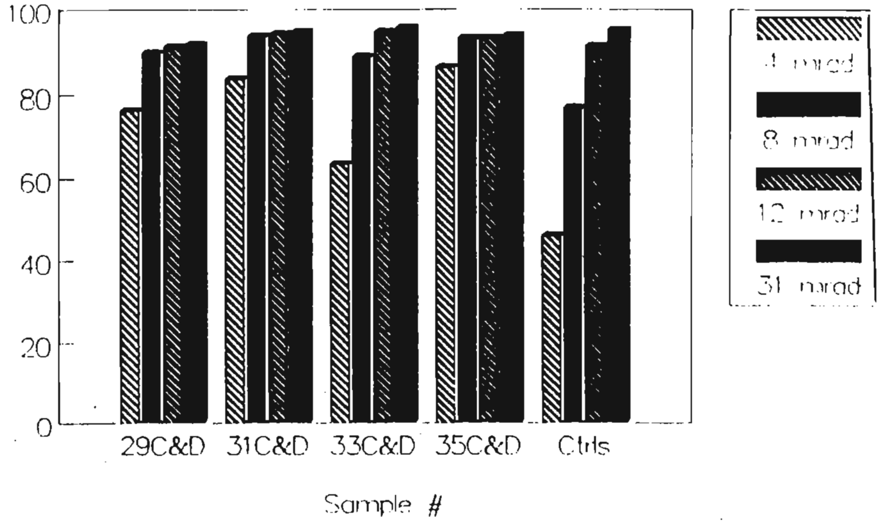

Figure 21. Summary of reflectivities at various cone angles for ECP-300A films treated with one and three layers, respectively, of 7F10HITc (Samples 29 and 31), and one and three layers, respectively, of L-10089 (Samples 33 and 35) (from Ref. 43). Samples had been subjected to 20 cycles of the SERI soiling-cleaning protocol.

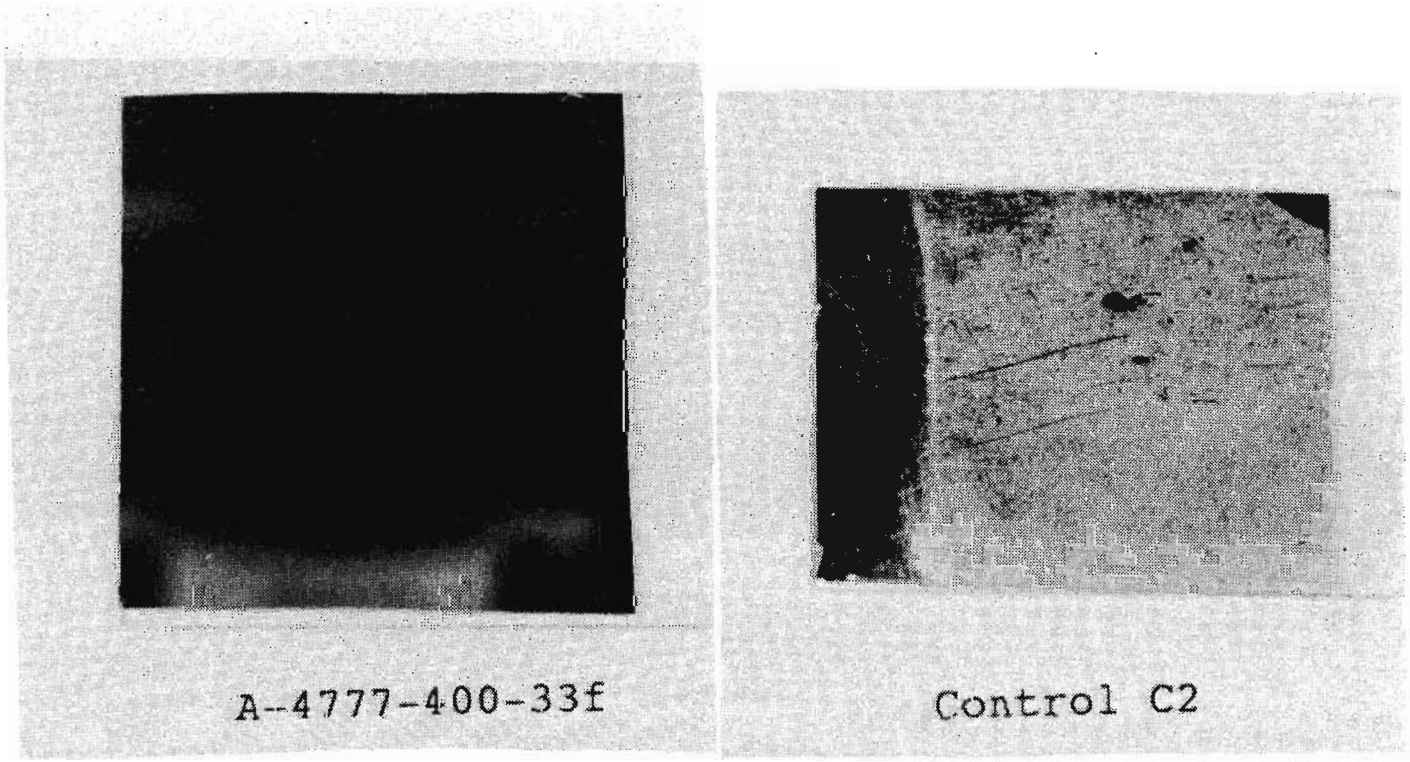

Figure 22. Photographs of (a) ECP-300 silverized polymethylmethacrylate LB-treated with fluorinated compound L-10089 and (b) an untreated control sample. Both have undergone the smearing, drying, and rinsing steps of the "mud-pack test;" the resistance to soiling of the treated sample is demonstrated by its reflection of the camera (from Reference 43).

19. APPLICATIONS OF SOLAR ENERGY TO SURFACE MODIFICATION PROCESSES

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ABSTRACT

Recent work at the National Renewable Energy Laboratory (NREL) has demonstrated the utility of using highly concentrated solar radiation to carry out surface modification processes. This highly concentrated radiant energy provides a controllable means of delivering flux densities of up to 10^4 W/cm^2 to solid surfaces. The resulting thermal energy can cause phase changes, atomic migrations, and chemical reactions on a surface without greatly perturbing the bulk properties. It is also possible for the photons to directly interact with species on the surface to carry out photolytic reactions. These changes result in improved material properties either by making the surface harder, more corrosion- or wear-resistant, and thermally resistant, or by giving it lower coefficients of friction than the base material, depending on the change produced. In a solar furnace, this flux can be delivered in large quantities over large areas or can be tailored to match the demands of a particular process. Furthermore, this occurs without the environmental liability associated with providing power to more conventional light sources. At NREL, fluxes in the range of 100-250 W/cm^2 have been used to induce beneficial surface transformations. Significant results have been obtained in the area of phase-transformation hardening of steels and melting powders and preapplied coatings to form fully dense, well-bonded coatings. Composition, hardness, and microscopy data are discussed, and advances in coating technology using highly concentrated solar beams to induce chemical vapor deposition and other processes are described.

I. INTRODUCTION

It is economically and ecologically attractive to modify the surfaces of materials using directed energy beams. Compared to bulk processing, this technique conserves materials and energy. For example, ion beams are used either to erode surfaces in prescribed ways or to implant species into a solid lattice [1-4]. Electron and photon beams are used to facilitate surface reactions and to supply thermal energy to surfaces to melt thin-film regions for annealing or welding applications [5-8]. The rapid growth in these areas of surface modification results from dramatic improvements in the quality and reliability of beam sources and from our increased knowledge and understanding of the fundamental nature of the systems. As a result, many products have been significantly improved.

Materials processing using directed energy beams is an energy-intensive endeavor. Conventional surface heating processes require converting primary energy (fossil fuels) to heat, heat to electricity, and electricity back to heat. A number of surface processing techniques require an additional step of converting electricity to radiant forms to be applied to the surface of a material. Generation and transmission losses account for a substantial amount of the original energy resource and can contribute significantly to operating costs for some applications. Further compounding this situation are the environmental liabilities associated with producing this energy with fossil fuels. These liabilities can largely be avoided for applications that are suited for surface processing in a solar furnace, in which no fossil fuels are needed and radiant energy can be used to heat surfaces directly. Solar energy has been explored as a bulk processing energy source for years. However, only recently has it been realized that the main contribution of solar energy to materials processing may be in the realm of surface modification. Some of the applications of directed energy beams now being used or considered have solar counterparts. In this article, we review areas of recent work in solar induced surface transformation of materials (SISTM) and point out where solar energy may have other interesting applications.

The National Research Council recently summarized its evaluation of the status of materials science and engineering in the United States [9]. The council found that materials science represents an "enabling" technology that is on the verge of unprecedented progress in a number of exciting areas, but the U.S. position in "synthesis and processing" and "processing performance" is relatively weak. The need to develop new synthesis and processing routes, coupled with increasing energy costs and increased environmental pressures, suggests that it is time to explore some nonelectric applications for highly concentrated (> 100 W/cm^2) solar radiation in the area of materials processing.

Modern solar furnaces range greatly in size and total power deliverable to a surface. Table 1 lists some solar facilities and their capabilities. The basic features of solar furnaces are exemplified in the recently constructed solar furnace at NREL, illustrated in Fig. 1. All solar furnaces direct the sun's radiation to a focus. There is, however, considerable flexibility in designing the optics to accommodate and optimize a variety of process parameters. Beams may be designed to accommodate irregular shapes, focal lengths can be adjusted to mitigate damage to the optical elements by sputtering or outgassing of

Table 1. Some High-Flux Solar Facilities

Location	Total Power (kW)	Peak Flux (W/cm^2)
Albuquerque, NM		
CRTF[1]	5000	240
Furnace	22	300
Atlanta, GA		
Furnace	1.3	950
Golden, CO	10	2100[2]
White Sands, NM	30	360
Odeillo, France		
Horiz. Furnace	1000	1600
Vert. Furnace	6.5	1500
Rehovot, Israel		
CRRF[3]	290	—
Furnace	16	1100
Uzbek, USSR	1000	1700

[1] Central Receiver Test Facility

[2] Average flux measured at the exit aperture of a nonimaging secondary concentrator

[3] Central Receiver Research Facility

the target materials, and a variety of secondary concentrator configurations are possible to adjust the flux levels to the most useful range for carrying out a processing step. It is possible to concentrate the solar radiation to about 2000 W/cm^2 with a single imaging concentrator, and up to 10,000 W/cm^2 with nonimaging concepts in a medium with an index of refraction greater than 1 [10]. An additional benefit is that scaling to very large power levels is possible. The Central Receiver Test Facility at Sandia National Laboratories in Albuquerque is capable of delivering 5 MW of optical power on target. With such large power levels available, it is conceivable to process very large areas. The radiation is delivered directly on target, resulting in processes that are inherently clean and efficient. There is no need for auxiliary cooling at the optical source. Reaction chambers can be operated in cold wall processes, because the beam is delivered directly on target. These features suggest some interesting applications that will be discussed in more detail in subsequent sections.

SISTM operates with terrestrial solar radiation, which is essentially a 6000 K blackbody band of radiation extending from the near-ultraviolet portion of the spectrum (305 nm), through the visible portion (maximum at 700 nm), into the infrared (2500 nm). As Fig. 2 illustrates, many materials are better absorbers of visible radiation than they are of infrared radiation. Most materials absorb solar radiation efficiently, even without the use of special coatings or techniques. Thus, concentrated sunlight impinging on surfaces causes extremely rapid heating. Dvernykov has calculated the time required for a number of substances to reach their melting points when absorbing a flux of 2×10^3 W/cm^2 [11]. The values in Table 2 have been adapted from Dvernykov and reveal that a surface with low thermal diffusivity reaches its melting point quickly, allowing the bulk of the sample to remain below its melting point. Furthermore, upper layers of atoms in a solid can undergo rapid migration at temperatures that are approximately 60% of the solid's melting point in what has been termed two-dimensional melting [12]. Therefore, even much shorter times than those in Table 2 can be used to modify surfaces exposed to concentrated solar radiation, and a number of interesting surface modification processes are possible at the flux levels achievable with a solar furnace.

A. Solar Furnace

The solar furnace at NREL was completed in January, 1990, and it incorporates a number of interesting design concepts that allow it to be used in a variety of experiments, such as the detoxification of hazardous wastes and advanced materials processing (Fig. 1). The heliostat (A) has a 31.8 m^2 area, with a front surface ultraviolet (UV)-enhanced aluminum coating (0.5-mrad slope error, 0.1-mrad specularity, 92% solar weighted reflectivity). The primary concentrator (B) is composed of 23 hexagonal facets that are spherical mirrors ground to a 14.6-m radius of curvature. The facets comprise an area of 11.5 m^2 and are arranged so that the focal point is 30° off axis as illustrated in the drawing. The mirrors are ground to 0.2-mrad slope error and 0.1-mrad specularity and are front surface, UV-enhanced aluminum. At the target, 94% of the energy falls inside a 10-cm circle. The beam shape is Gaussian with a peak flux of 250 W/cm^2. A nonimaging secondary concentrator can be used to increase the peak flux to 2500 W/cm^2, and there are plans to demonstrate a refractive, nonimaging secondary that will raise the peak flux to over 5000 W/cm^2. The attenuator (C) is a vertically opposing two-plate design that trims the light arriving from the top and bottom concentrator facets as it closes. It is located 1.78 m from the focal plane, in the region of 2.5 W/cm^2 peak flux. The plates move with speeds adjustable in the range of 5 to 70 mm/s and are computer-controlled. Flux or temperature profiles can be programmed, and compensation for minor fluctuations in the solar insolation is possible. The shutter (not shown) is an air-actuated guillotine that can be operated in a manual or computer-controlled mode. It is located 35 cm from the focal plane, is actively cooled, and opens or closes in 0.5 s. In addition to these features, the long-focal-length primary mirrors allow flexibility in experiment size and orientation. There are remote video monitors with color cameras for real-time viewing of the target zone and flux mapping, and there are over 100 data acquisition channels for thermocouple, pyrometer, weather, and insolation data.

Table 2. Calculated Heating Rates

Material	Melting point, T_m (°C)	Time to reach T_m (S)[1]
Metals		
Al	660	0.42
Cu	1083	3.10
Ni	1453	1.03
Steel	1535	0.79
Ti	1670	0.23
Cr	1857	1.46
Mo	2617	4.70
W	3407	9.80
Oxides		
SiO_2	1720	0.014
TiO_2	1870	0.044
Al_2O_3	2050	1.00
V_2O_3	2410	0.107
CaO	2580	1.66
HfO_2	2780	0.188
MgO	2800	2.59
ZrO_2	2900	0.089
Carbides		
TiC	3200	9.14
NbC	3500	0.86
ZrC	3540	0.112
SiC	3830	0.56
Nitrides		
Si_3N_4	1900	0.059
AlN	2200	1.32
BN	3000	0.545
TIN	3200	0.611

[1] Time required to reach T_m while absorbing a flux of 2000 W/cm^2

B. Target Assemblies

One result of the material processing work at NREL has been the fabrication of sample chambers and related equipment designed specifically for material processing using a concentrated solar beam. Among the equipment necessary for an experimental materials processing facility, NREL has installed an xyz platform for translating specimens, a rotatable mirror that redirects the solar beam onto horizontal surfaces, an optical laser pyrometer to accurately measure and control sample surface temperature, low-power alignment lasers, and secondary concentrators to increase the available flux densities. Sample chambers include designs for maximizing temperature gradients by cooling the backside of the sample with forced air or water, and chambers that allow control of the sample atmosphere. The most sophisticated sample chamber to date includes a four-gas mass flow control system connected to a sample chamber whose pressure can be controlled dynamically with a butterfly valve backed by a two-stage rotary pump. The chamber can also be pumped to a pressure of $< 1.0 \times 10^{-7}$ Torr by a turbo-molecular pump, and the chemical species in the sample chamber can be monitored by residual gas analysis. A wide variety of experiments can be accommodated with the current hardware, and many more are possible with relatively minor fixturing.

II. SOLAR ADVANTAGES

There are a number of advantages to using solar radiation for the surface processing of materials. Some of these were mentioned in the Introduction. Primarily, radiant sources of energy are well suited to surface modification because the energy is converted to heat at or near the surface, where it is used directly. The resource is matched to the process. This conserves energy and affords the possibility of minimizing cost. Furthermore, solar radiation need only be directed and focussed, not converted to other forms. There are no generating and transmission losses. The processes are inherently efficient and carry little environmental liability. Otherwise, using solar radiation is very similar to using other light sources (lasers, high-intensity arc lamps, or infrared heaters) for transient thermal processes. The primary advantages are as follows:

- The radiation is supplied in a broad spectral range, where most materials absorb efficiently without special coatings. High heating rates are possible.
- Because the beam is delivered on target without prior conversion processes, there is little waste, efficiency is high, and there is usually no requirement for auxiliary cooling.
- Scaling to very large powers and large areas is straightforward.
- The optics for a particular process are ordinary and can be designed with long focal lengths. This makes sample areas flexible and manipulation convenient, and it reduces fouling of the optical train. It is also easy to shape the beam and control the pulse to the target zone.
- There is minimal environmental impact in using this technology.
- The spectral range of the radiation is 0.305 to 2.5 μm. It is possible to stimulate a number of interesting photolytic processes on material surfaces.
- Systems analysis indicates that, depending on the location, the cost of energy delivery is less than that of more conventional techniques.

The primary disadvantage is that a solar furnace requires good, direct normal insolation. This means that it doesn't work at night or on an overcast day. Consequently, one must either be very smart about the use of labor during these periods, or have a hybrid operation.

III. DEMONSTRATED AREAS OF APPLICATION

A. Transformation Hardening of Steels

The process of transforming steel to martensite is called "transformation hardening." For some applications, it is desirable to have a hard wear-resistant surface with a softer, ductile subsurface. To achieve this end, it is necessary to preferentially heat the surface. Typical methods of applying heat to the surface include flame, induction, or laser heating. One of the most recent techniques for surface hardening of steel—laser transformation hardening—is now being used by the automotive industry for engine and drive-train components. This acceptance of laser transformation hardening was an encouragement to develop the data base for the solar hardening of steel. Experimental confirmation of surface hardening of steel using concentrated solar radiation and a favorable economic comparison between a laser facility and a solar furnace [13] encouraged an examination of this application for solar furnace technology.

Over the last 8 years, considerable research has been conducted on surface hardening by solar energy [14-21]. The literature reveals that workers in China accomplished most of this work, but one report was published in the Soviet Union [22]. The solar furnace used in China is a 1.56-m parabolic concentrator with a focal length of 663 mm and a 6.2-mm image at the focal point. A flux of 3000 W/cm^2 is claimed (calculated, not measured), with a maximum temperature around 3000°C (ZrB_2 melted). A hardened spot almost 5 mm in diameter was obtained with a 1-s exposure. Longer exposures enlarged and deepened the hardened region. The wear resistance of solar-hardened steel was compared with that of steel hardened by an undisclosed method. Superior wear characteristics of the solar-hardened specimen were attributed to the high intensity of heat at the surface, which gave a fully martensitic structure. Carbon was applied to the surface of some samples to increase the rate of heat absorption. Some relatively complex surfaces were hardened by a scanning process across the cutting edges of reamers and bits.

We have also experimented using solar furnaces in the United States to harden steels [23,24]. The solar fluxes available for our experiments were of somewhat lower intensities than those reported by the Chinese researchers. Consequently, the hardened zones in our work penetrated deeper into the surface and resulted in relatively thick transition regions between the fully hardened zone and the unaffected, soft substrate material. Transformation hardening experiments on tool steels were carried out in air at the solar furnace in Albuquerque. Samples 2' × 6" × 0.5" were mounted onto a frame and clamped to the positioning table. After the solar beam was directed onto the sample, it was translated in the z direction to obtain a strip of hardened material. To obtain more information from a single pass, the translation rate was maintained at a single value while the incident flux was varied as a linear function of position. Thermocouples were spot-welded at 2-in. intervals on both the front and back portions of the sample so the temperature of the piece could be monitored. Selective hardening of the 4340 tool steel occurred in the range of 200 W/cm^2 at scan speeds in the range of 0.5 mm/s. The fully hardened region was 1-2 mm in depth and approximately 2 cm in diameter, with a heat-affected zone penetrating another 4-5 mm into the plate (Fig. 3a). The hardness decreased from the fully hardened zone to the unaffected bulk region smoothly as shown by the graph of microhardness (Fig. 3b). The unaffected zone was completely unhardened, just like the material as supplied from the manufacturer. For massive targets such as these, further work at 200 W/cm^2 would be fairly uninteresting. Based on mathematical modeling, we have postulated that the scan rate can be increased and the depth of hardening reduced by increasing the solar beam intensity by a factor of 5. Figure 3a shows the overall shape of the hardened region, which follows the gaussian distribution of the incident flux. A flat beam shape would result in a more uniform hardened region. Modeling work at NREL has demonstrated that solar furnaces can be constructed to create flat beam shapes, as well as more exotic figures.

In other experiments, nitride-grade steel samples, 89 mm in diameter and 6.4-mm thick, were exposed to the solar beam under a controlled atmosphere of either nitrogen or argon, using the previously described vacuum sample chamber, and were water cooled from the backside to increase temperature gradients and to decrease quench times of the heated sample. They were exposed to fluxes up to 185 W/cm^2. Hardening was observed at the higher fluxes but was not uniform at the surface. Instead, there were hardened dendritic-like needles beginning on the surface and extending 2 mm into the bulk. The transition zones in this case were sharp. Regions on the surface between the fully hardened needles were only partially hardened, indicating a nucleation phenomenon for the hardened zones. This nucleation and growth phenomenon is expected for the austenitic transformation and is a function of both the temperature and the composition of the steel. Because the nitride-grade steel contains less carbon than the tool steel, it is expected to show more resistance to nucleation. Using a more intense solar beam and elevating the surface to a higher temperature would produce a fully hardened localized region at the surface.

B. Cladding of Preapplied Powders

It is sometimes desirable for the surface properties of a material to exhibit particular properties, which may either be incompatible with desired bulk properties or cost-prohibitive to achieve throughout the part. To overcome these problems, techniques such as plasma spray coating, laser melting of powders, and shock cladding have been developed to apply desired coatings to a material surface. Although these techniques can apply a powder or other forms of material to a surface, it may be necessary to postprocess these films to improve the adherence of films to the substrate, close or mitigate porosity, or cause solid-state chemical reactions to take place in the film to form the desired phases. A solar furnace can be used to melt powders onto substrates as well as postprocess films applied by other means.

Soviet scientists have already demonstrated that slip coatings can be melted onto substrates in a solar furnace [25]. These coatings of fine powders have the advantage of strongly absorbing the solar radiation, thus making the process more efficient. The coatings were melted onto steel and titanium alloys to produce coatings 50-150-m thick. The coatings had two general compositions, TiC-Ni-B and WC-Ni-B, and were wear- and corrosion-resistant. A 2-m diameter SGU-5 solar furnace was used to expose the samples at 600-1200 W/cm^2. The coatings interacted with the substrate by diffusion, with most of the volume of the substrate remaining unchanged. The coatings had satisfactory surface qualities, good density, a framework structure, and good bond strength between the coating and substrate. The report summarizing these findings was considered a proof-of-concept demonstration, and work at NREL was conducted to corroborate and expand these concepts. We have experimented with a number of preplaced powders using the solar furnaces at Sandia National Laboratories and NREL [26]. In the existing furnace designs, the sample surface is perpendicular to the ground and therefore parallel to the forces of gravity. This resulted in some difficulty in obtaining consistent melts, because the powders tend to fall off with increasing temperature. We have recently installed a turning mirror at the NREL solar furnace, allowing easier manipulation of the sample surface and improved control over the process.

Even given the difficulties associated with the older sample mounting system, we were able to achieve excellent results. Using a technique in which powder is impregnated with polymethylmethacrylate (PMMA) by diffusing a solution of PMMA in methyl ethyl ketone (MEK) into the powder layer, we clad a number of different alloy powder types onto 4340 and 1040 steel. Figure 4 is a set of micrographs illustrating effective clads with a wide variety of alloy powders. These claddings were formed with a range of exposure conditions, but we found that fluxes in the range of 100 W/cm^2 produce very effective coatings. These micrographs support the observation that the melted powders form excellent metallurgical bonds with the substrate layer and that the clad material exhibits a high degree of densification. X-ray diffraction studies have confirmed that the desired metallic and intermetallic compounds were either preserved or formed in all cases.

The results from our studies and the Soviet experiments suggest other applications. For example, consider coatings for dissipating heat in high-temperature systems. Some example emissivity agents used in thermal protection systems (TPS) are SiC, SiB_4 and $MoSi_2$. These materials efficiently radiate heat, thus reducing the flow of heat into the substrate. Coatings of these materials have been applied in the metal and refractories industries and are now being used in the aerospace industry. Energy use has been reduced by an average of 24%-38% for the refractories industry. Difficulties have been experienced in applying the emissivity agents in TPS coatings to carbon-carbon materials, according to Fisher [27].

Composites are another class of materials in which good applications for solar processing exist. Carbon-carbon materials are currently used as the heat shield for the space shuttle nose cap and wing leading edges. Carbon-carbon materials are also contenders for various high-temperature parts of aircraft turbine engines, such as exhaust nozzles in which high strength-to-weight ratios are important. Reducing both the heat and the rate of oxidation of the carbon-carbon materials is extremely important. Silicon-based coatings are being explored because they produce SiC with good emissivity, as well as other silicon compounds, like SiO_2, that have good oxidative stability. For example, Smialek [28] reports that slurry mixtures of aluminum and silicon powders in a nitrocellulose lacquer vehicle can be fused onto carbon with some success. Fusion times of up to 2 h at temperatures in the range of 1300°C were used to produce the fused coatings. Problems included aluminum vaporization, porous external surfaces on some samples, and thin coatings on other samples because the coating infiltrated the pores (leaving a much thinner than anticipated outer layer of $< 25\ \mu m$ in thickness). Using SISTM to process coatings similar to these might reduce process time, minimize vaporization, and increase the smoothness of the coating. Similar coatings are being explored for use on an aero-assisted orbital transfer vehicle [29]. Concentrated solar energy has been used to react layered Si_3N_4-C and BN-C systems to form SiC and B_4C between the layers [30], demonstrating that such SISTM techniques are possible.

C. Self-Propagating High-Temperature Synthesis (SHS)

An interesting observation related to powders might be added at this point. It has been demonstrated that some mixtures of powders will react with the release of energy. Once initiated, the exothermic reaction becomes self-sustaining and will propagate through the reaction mixture. This is called self-propagating high-temperature synthesis (SHS) [31,32]. We have found that SHS can be initiated in a solar furnace. Powders of Al and Ni have been mixed and bonded to substrates, and multiple layers of vacuum-deposited thin films have been placed on targets. Both types have been exposed to thermal pulses in the solar furnace. When reacting, such powders and films add their heats of reaction to the solar beam, allowing temperatures to reach the melting point of refractory metals and ceramics. High-quality thin films with very narrow heat-affected zones can be produced in this manner (Fig. 5).

Modern high-performance ceramics offer unique combinations of properties that make them attractive materials [33-35]. Processing techniques are of utmost importance when high temperatures and stresses are encountered. Indeed, developing novel techniques for coating and joining ceramic composites is listed as one of the future needs in the ceramic industry [36]. Fisher [27] recently reviewed applications of ceramic coatings requiring retention of mechanical properties at high-temperature, tribological properties, and corrosion resistance to high-temperature fluids. The use of SISTM to initiate and sustain the SHS processes to produce these coatings is an interesting possibility.

D. Plasma and Flame Sprayed Coatings

Plasma- and flame-sprayed coatings are widely used throughout industry, and the techniques have recently been reviewed [37]. A significant problem encountered by researchers using these techniques is the porosity of the coating. This porosity results in less than optimum corrosion resistance on many metal components. Also, cracks are initiated and propagated along these voids, resulting in delamination and failure. Laser-beam treatment of these coatings has been somewhat successful [38] but is known to produce cracking [1]. A logical extension of the solar melting of powders previously described is to use solar beams to remelt and densify preapplied plasma- or flame-sprayed coatings. Preliminary work to explore this possibility is under way.

E. Films Produced by Physical Vapor Deposition (PVD) Methods

Various physical deposition methods can be used to produce layers of selected films on substrates. Subsequent heating of these layers can result in the production of the desired coating either by solid-state diffusion and reaction or by melting and liquid diffusion and reaction. The process has been used to produce compound semiconductor films by direct synthesis from layers of the constituent elements deposited on insulator substrates [39]. The stoichiometry of the initial layers can be adjusted by the composition, relative thickness of each layer, and number of layers of each composition deposited in the original sample. Some example compounds prepared this way are AlSb, AlS, CdTe, CdSe, ZnTe, and ZnSe. A typical energy source for this type of process is laser irradiation. The small size of the laser beam results in the melting of small portions of the sample at a time. Although useful in producing electronic devices, laser irradiation is more difficult to justify for large structural applications. For this reason, a solar beam with large deliverable energy and a relatively wide spot diameter may prove to be an effective alternative to a laser or other similar processing source. We have carried out preliminary studies into intermetallic compound formation using various combinations of aluminum and nickel layers, which form nickel aluminides with excellent high-temperature and corrosion-resistant properties. The initial set of diffusion bonding SHS reaction experiments were carried out in air, and samples were water cooled on the back side of the sample surface. The various combinations of Ni and Al layers were sputtered onto 4340 steel and pure iron targets using a magnetron sputtering unit. The outer coatings were aluminum, to increase oxidation resistance during the test. However, the high reflectance of aluminum made energy transfer inefficient. Applying carbon to the surface of some coatings reduced exposure times. The reactions were followed by optical pyrometry and by visually monitoring the sample surface with a remote video system. X-ray diffraction studies conducted after samples were exposed to the solar radiation demonstrated conclusively that it was possible to form the desired intermetallic phases.

IV. CURRENT RESEARCH AND DEVELOPMENT

The electronics industry has developed extremely sophisticated surface modification techniques, and some of these are candidates for large-area applications. Techniques that are being examined for SISTM applications include chemical vapor deposition (CVD) and its variations, rapid thermal annealing (RTA), and zone-melting recrystallization (ZMR). These surface modification techniques are not exclusive to the electronic materials industry. For example, CVD is an exceedingly important method of creating advanced materials and coatings. Applications of CVD are found in the fabrication of electronic components, fiber-reinforced composites, corrosion-resistant coatings, and coatings in the tool industry. A recent review examines the use of CVD in these and other applications [40].

A. Chemical Vapor Deposition

Broadly defined, CVD is the formation of solid products from the chemical reaction of gaseous reactants on or near surfaces (see Chapters 12 and 13, this volume). It is important to note that all of these reactions are initiated by heat and/or radiation. CVD reactor units can be classified as either hot-wall or cold-wall systems. Hot-wall reactors are modifications of a typical furnace through which the reacting gases pass. These reactors are commonly used but suffer from inefficiency because chemical reactions take place on other heated surfaces in the reactor system (in addition to the sample). Cold-wall reactors concentrate the reaction activation energy on or close to the surface to be coated by using induction heating or radiant energy from such sources as lasers and arc lamps. Solar furnaces fitted with CVD reaction chambers are very good cold-wall reactor systems. The sun's radiant energy can be nicely controlled to deliver prescribed amounts of heat for predetermined time periods. The systems are very clean and energy efficient. In addition to thermal activation from the solar beam, there is the possibility of photolytic activation if the chemical systems contain an absorption band in the high energy portion of the solar spectrum. The production of TiN, TiB_2, SiC, and hard carbon films using a solar furnace is being explored at NREL. Based on a limited amount of work accomplished to date, relatively small solar fluxes are required to produce CVD films. Films could be applied to large areas using this technique.

The solar furnace may also be used for rapid thermal chemical vapor deposition (RTCVD), a process that normally uses radiant heating lamps in combination with a CVD chamber. These reactor systems are capable of rapidly heating surfaces for short periods of time to deposit thin films. Such RTCVD reactor systems are being developed in the electronics industry to produce high-quality films of Si, SiC, and Si_3N_4 [41,42].

B. Rapid Thermal Annealing

Ion implantation techniques are desirable in the semiconductor industry because the quantity and depth of carrier moieties can be precisely controlled (see Chapter 15, this volume). Traditionally, defects produced by ion implantation have been annealed out in furnaces. Temperatures of 900°-1200°C are used for silicon samples, and temperatures of 800°-1000°C are used for GaAs samples. The annealing temperature is uniform throughout the whole wafer because the sample is held at these temperatures for 15-30 min. Unfortunately, under these conditions, dopants can undergo extensive redistribution. This makes it difficult to fabricate shallow junctions and small devices for very large scale integration (VLSI) circuits. To reduce the annealing time, three different transient-annealing techniques have been introduced. These techniques are pulsed laser or electron beam, scanned laser or electron beam, and RTA with incoherent light. For reasons outlined in an article by Fan [43], the RTA process is the most desirable of the three. The RTA process uses radiative heat sources such as tungsten-halogen lamps and annealing times of 1-10 s. These conditions are remarkably similar to those found in the high-flux region of a solar furnace. The application of SISTM to annealing ion-implanted surfaces may have advantages that are unanticipated at this time. SISTM should even be applicable in the production of solar cells [44,45].

RTA work in progress at NREL is directed toward using the solar furnace to produce high-temperature superconductor films on substrates such as $SrTiO_3$, ZrO_2, and MgO. The films are produced by metalorganic deposition and are subsequently treated by an RTA process in a solar furnace to produce the superconducting phase [46,47].

C. Metalorganic Deposition

Metalorganic deposition (MOD) technology is a rapidly growing alternative to CVD techniques for forming certain types of thin films on solid substrates. Research at NREL has concentrated on high-quality, high-critical-temperature (T_c) superconducting films and metal films that can be grown on various substrate materials using this technique. Optical coatings are another area of interest, but these have not yet been studied in this laboratory. A key step in producing the highest-quality films is RTA in a controlled atmosphere. The ability to control the thermal pulse simultaneously with the atmosphere, and thereby control the properties of the resulting films, offers the possibility of tailoring the films for specific applications.

For the superconductors, MOD followed by an RTA in a solar furnace has two distinct advantages over the more conventional approaches. The MOD technique produces films of great uniformity and high critical current densities, because the precursors are mixed at the molecular level and are easily adjusted to produce exact stoichiometry. Reacting the precursor material in an RTA process can orient the grains with respect to the substrate and provides access to phases not available with normal thermal treatment. With a solar furnace, it is possible to scale up the area of rapid thermal processing to any practical size by designing the optics of the furnace for that application. Furthermore, it will be possible to explore the effects of using optical fluxes that are up to two orders of magnitude larger than those obtainable with commercial RTA equipment.

D. Joining

Certain geometries are difficult to join, because there is a mismatch in the coefficient of thermal expansion of materials, because the particular structure of the pieces cause warpage upon heating and cooling, or because there are heat-sensitive parts in the assembly. In some cases, these problems can be overcome by using radiative heating to make the desired joint. The joint is made by applying heat just in the region of interest by sweeping the beam along an appropriate seam. We are engaged in work that addresses making joints in castable alloy figures of peculiar shapes and in ceramic pieces in which parts of the assembly contain heat-sensitive components. Preliminary investigation indicates that the radiative joining technique with the solar beam will work well for these applications.

V. FUTURE DIRECTIONS

Solar furnaces may have applications in a number of interesting areas of materials science and surface processing. Relatively new and exciting topics include the production of nanophase materials, the rapid thermal treatment of ceramics and composites, and chemical vapor infusion. Some other areas of interest are described in the following sections.

A. Electronic Materials Growth and Processing

A vacuum system with a window and flow control for gases, combined with an intense solar beam provides excellent control over process conditions. The beam allows fast thermal ramping of the target in a cold-wall reactor, and the mass flow system provides the ability to rapidly change the process gases over the target. Thus, RTCVD can be combined with diffusional steps or used by itself to grow multilayered electronic materials. Where the desire is to grow large-area semiconductor materials, as in photovoltaic panels, and where the energy costs are a substantial fraction of the overall processing costs, there may be good reason to investigate the possibility of using solar technology to accomplish the film growth. For certain applications, such as the growth of extremely low-defect single crystals in a microgravity environment, concentrated solar radiation may be the only energy resource that can be used [48].

B. Zone-Melting Recrystallization

Graphite heaters [49] or lamps [50] have been used to scan across multilayered samples deposited on substrates such as silicon, germanium, or sapphire. Heating an intervening layer, typically a fine-grained silicon film, causes it to convert slowly to a recrystallized silicon film at a scan rate of 1 mm/s. This ZMR technique creates large-area films and may provide excellent substrates for the epitaxial growth of GaAs [51]. The ZMR processes described may possibly be carried out using SISTM. These processes represent interesting areas for further development.

C. Weather/Space

Effectively operating a solar furnace facility requires a good resource of direct normal radiation. In the continental United States, a location within a five-state area (including Arizona, Colorado, Nevada, New Mexico, and Utah) or in a portion of one of the bordering states is essential. The facility cannot operate during the night or during periods of dense cloud cover. Consequently, a facility must be sized to provide the required throughput during the available hours of operation, and the prudent use of labor is mandatory. With these considerations as ground rules, it is possible to compare the cost of processing with a solar furnace to the cost of processing with more conventional tools.

Systems studies were performed to compare the performance of appropriately designed solar furnaces for a generic materials processing task to that of the more conventional techniques using lasers and arc lamps. These analyses indicate that for sites with good insolation and batch processing, the solar furnace is extremely competitive [13]. In fact, moving to larger fluxes and larger total powers, the solar furnace economics become progressively more favorable as larger fluxes and total powers are employed. This is because capital equipment costs and power consumption become more important and labor costs become less important as the size of the facility increases. Light is reflected once or twice during concentration, giving losses of 5% to 10% at each reflection, but there are no energy conversion losses. Other optical power supplies typically convert the heat obtained from the combustion of fossil fuels to electricity and then must convert the electrical energy into light. The overall efficiency of using electricity derived from fossil fuels is approximately 9% for high-pressure arc lamps and 4% for CO_2 lasers.

As interesting as these arguments are for terrestrial applications of solar furnace technology, they become even more compelling for space applications. First, there is 70% more power density from radiation in space than there is terrestrially because of the lack of atmospheric attenuation [52]. This figure assumes 1367 W/cm^2 mean direct normal radiation at earth orbit and air mass 0, versus 800 W/cm^2 direct normal availability at air mass 1.5 for the southwestern United States. Second, there are more UV radiation and shorter wavelengths for any mission that requires photolysis. Additionally, direct concentration of the solar resource is the most efficient way to apply large optical fluxes to a target. For example, a 1-m^2 dish could deliver about 1 kW of optical power to a target. It would take at least an additional 10 m^2 of collector area to supply the electricity to operate an arc lamp, or an additional 25 m^2 of collector area to supply the electricity to operate a CO_2 laser. In addition, there is the problem of waste heat rejection. Certainly, some processes can be carried out without the need for radiant energy. In these cases, it is probable that other energy sources would look attractive. In low earth orbit, where a satellite is regularly in the shadow cone of the earth, or for a deep space probe, where there is a diminishing amount of solar radiation to use, other energy sources are required. Nevertheless, there are many missions for which a solar concentrator would be worth serious consideration.

A number of significant applications exist for solar concentrator technology in space. These include cleaning of the wake shield and fixtures in the materials science experimental and processing areas, supplying energy for a number of materials processing tasks (requiring heat and light), fabricating and repairing structures, mining and manufacturing on the moon, treating and recycling human and operational waste materials, and generating electrical power. All of the direct applications are particularly interesting because they use the energy delivered in the solar beam without intermediate conversion to electricity. This implies improved efficiency, reliability, and economy. More detail about these ideas is given elsewhere [53].

VI. CONCLUSIONS

Directed energy beam processing is an innovative and rapidly growing method for surface modification. Ion beams, electron beams, and laser radiation each have their advantages and disadvantages. Highly concentrated solar radiation is an additional option that has some features not easily produced in the other energy beam sources; consequently, it is also being explored as a surface processing tool. Because solar energy can rapidly deliver large amounts of heat to a surface, this heat can be used to induce transformation hardening, surface alloying, and CVD. The suggested applications presented here constitute examples of whole areas of SISTM that could be explored. Given the scope of the surface processing field, we can expect that other applications will emerge. This article deals only with surface processing technologies that seem to be a good fit to the solar resource. No mention is made of the areas of basic research into the chemistry, physics, and metallurgy of materials in the high-temperature, high-solar-flux environment. Work in the surface chemistry of materials exposed to highly concentrated solar energy reveals interesting processes that modify the surface composition of alloys [54-56] and implies photolytic enhancement of surface reactions. These possibilities for SISTM are just beginning to be explored. We hope that the potential applications presented in this paper will stimulate additional ideas and interest in the field.

ACKNOWLEDGMENT

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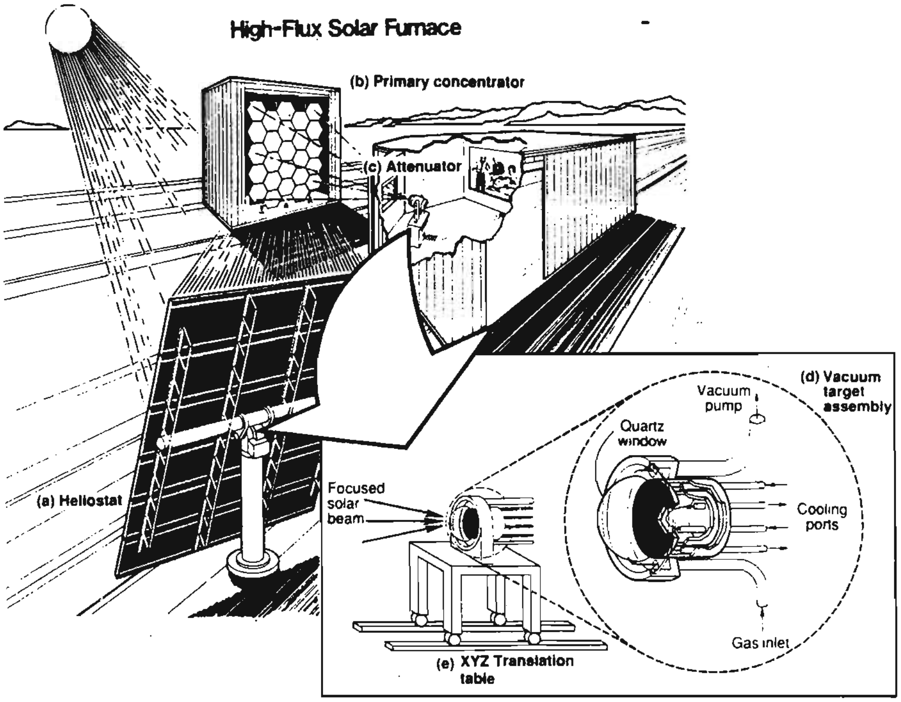

Figure 1. High-flux solar furnace located on South Table Mountain, Golden, CO. (a) Heliostat, (b) Primary concentrator, (c) Attenuator, (d) Shutter, and (e) Vacuum target assembly.

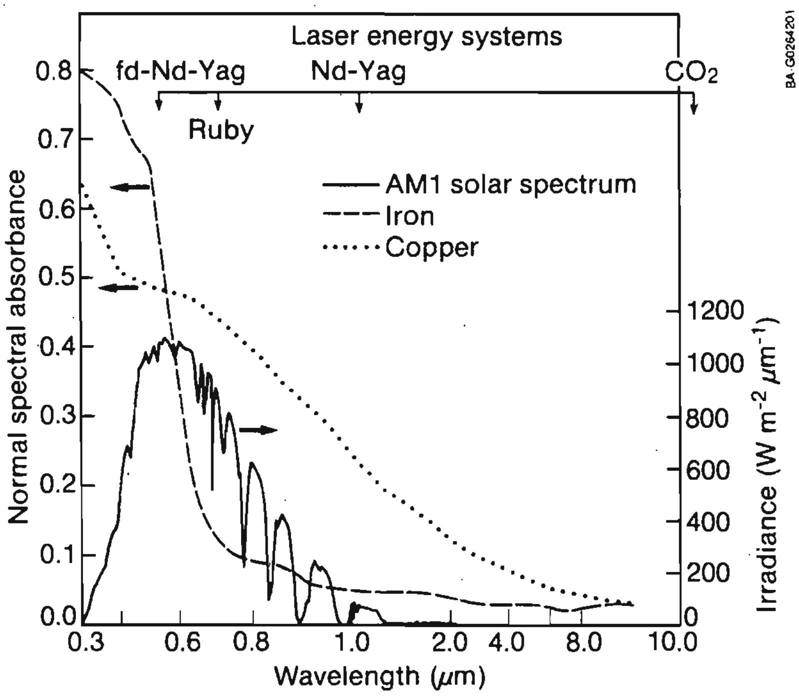

Figure 2. Power density in the solar spectrum. Superimposed are the absorption spectra of Fe and Cu and miscellaneous laser lines for comparison.

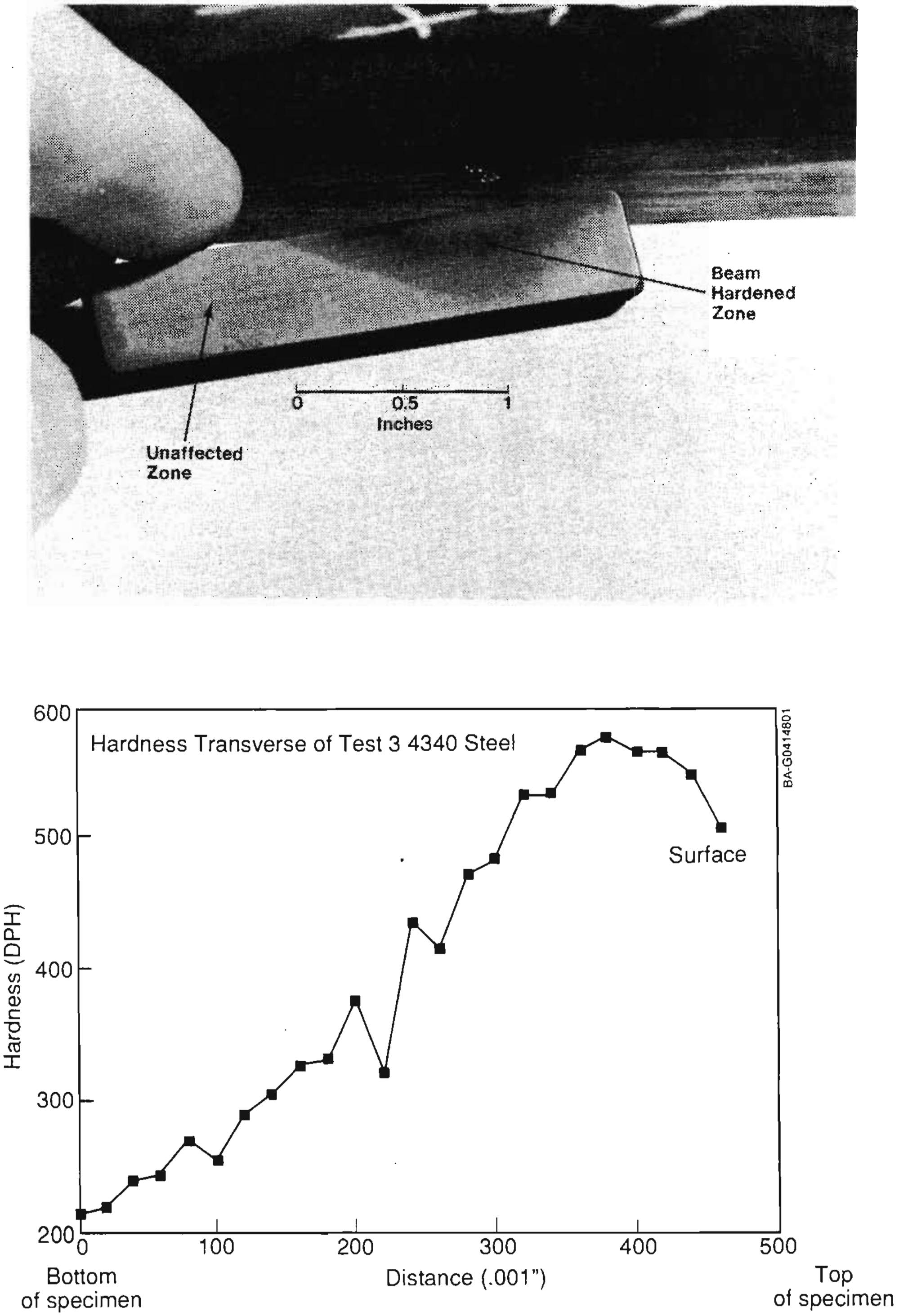

Figure 3. (a) Macrophotograph of solar hardened tool steel. Photograph of the steel plate after exposure to the solar beam. (b) Microhardness data compiled on a hardened tool steel plate.

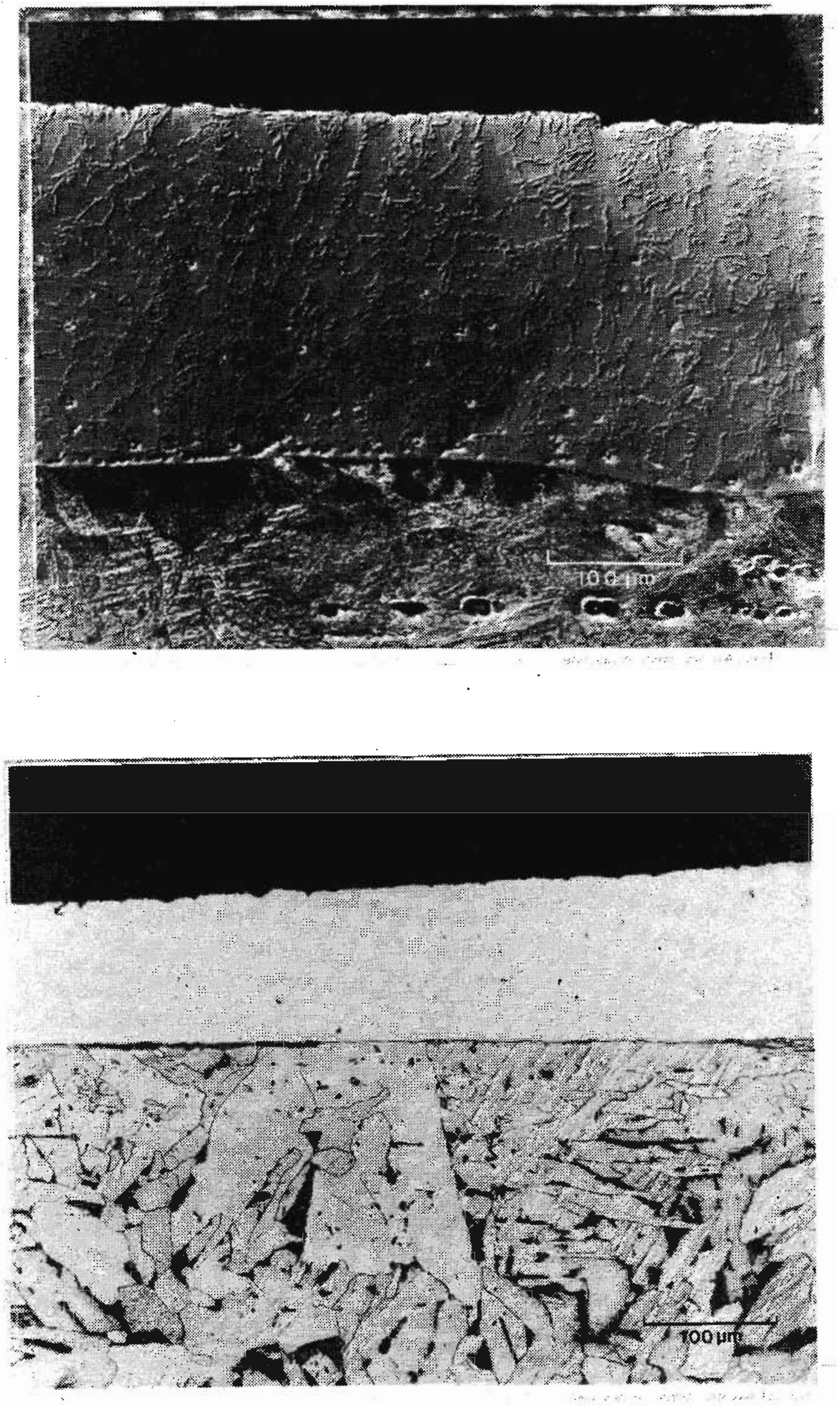

Figure 4a and 4b. Micrographs of various alloy powders melted onto steel substrates. Note the high density of the melted powder and the good metallurgical bonding between the coating and the substrates. (a) 761 (Ni/Cr/B) powder onto 4340 steel. (b) 316 SS powder onto 1040 steel.

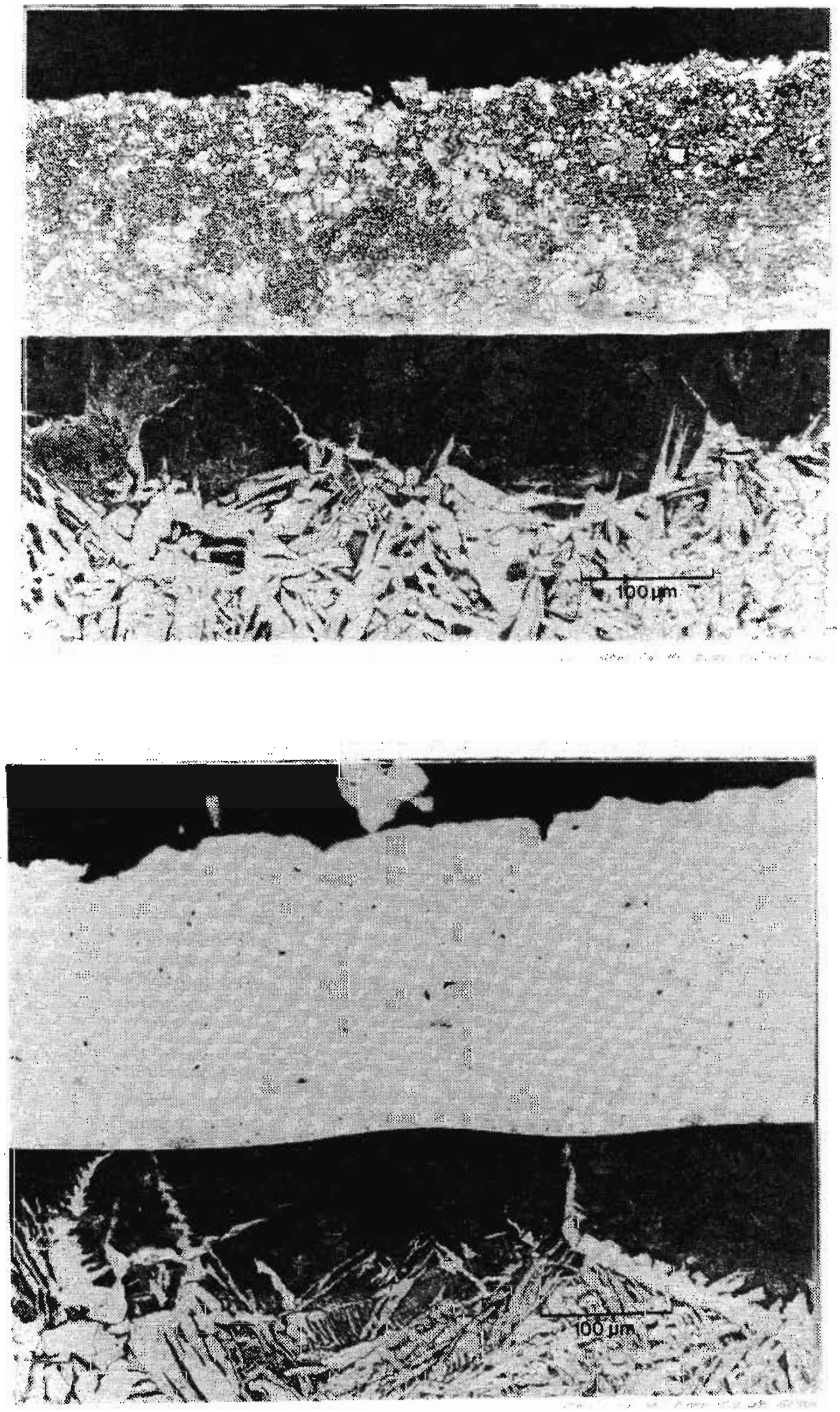

Figure 4c and 4d. Micrographs of various alloy powders melted onto steel substrates. Note the high density of the melted powder and the good metallurgical bonding between the coating and the substrates. (c) WC (6%) in Co onto 1040 steel. (d) Ni (95%) Al (5%) onto 1040 steel.

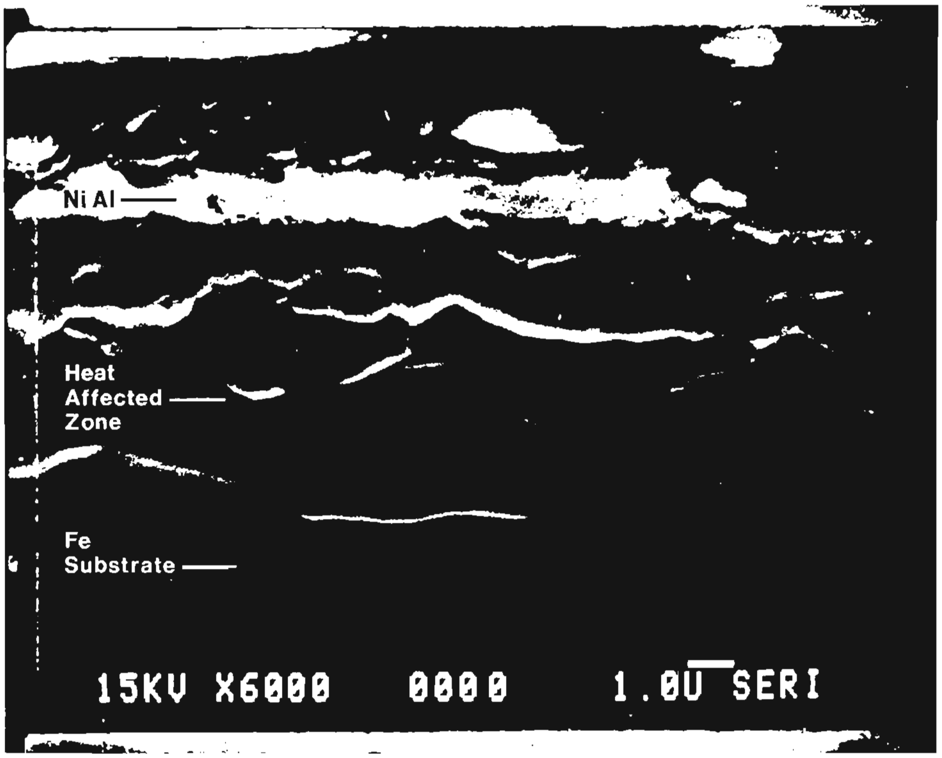

Figure 5. NiAl thin film on Fe substrate. The film thickness is 1 μm, and the zone affected by heat is about 7 μm.

20. PANEL ON CORROSION PROTECTION

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I. INTRODUCTION

Corrosion and materials degradation in transportation systems are major costs to society. In a 1987 National Materials Advisory Board report (Agenda for Advancing Electrochemical Corrosion [1]), it was estimated that the cost of corrosion of automobiles was $15 billion per year. The cost to all transportation systems, including trains, aircraft, and ships, is considerably higher, possibly as much as $30-$60 billion per year. While exact numbers are difficult to pinpoint, it is reasonable to assume that at least a third of this cost is avoidable through better design and engineering, appropriate education, and the use of currently available corrosion control technology. Accordingly, the avoidable cost of corrosion in the transportation sector of our economy alone might be as high as $10-$20 billion, which is more than the gross national products of many countries in the world community.

While the cost of corrosion is spread more or less uniformly throughout our society, the cost to transportation and, in particular, to road transportation systems, is of particular importance because of the manner in which these systems pervade our society at all levels. For example, one in seven jobs in our society is directly or indirectly related to motor vehicles; motor vehicles cost an average household $5,187 per year. An estimated 739,000 of these jobs are in the motor vehicle manufacturing sector alone, and many times this number is in ancillary sectors.

While other sectors of the transportation industry are not as large, they are, nevertheless, important to the health of our economy and to our financial and social well-being. Thus corrosion and materials degradation in the air, rail, and ship transportation industries together represent a capital investment that is a significant fraction of society's investment in road transportation vehicles; in some cases (e.g., air transportation), the corrosion-related failures can be catastrophic.

The goal of the "Corrosion Protection" working group was to review the current state of the art of corrosion science and engineering and corrosion protection technology in the transportation and utility industries, excluding nuclear, fossil, and hydroelectric power generation. Because the three excluded technologies represent by far the major components in electricity generation, we have chosen to emphasize the road transportation industry. As noted above, this industry represents a major activity in our society and is often regarded as a barometer of the health of our economy. Furthermore, the road transportation industry has a significant impact on everyone's daily life, and the damage caused by corrosion is evident to all. What is not evident, however, is the enormous cost of corrosion or the manner in which corrosion affects the safety of our road transportation systems. The purpose of the material that follows is to review the impact of corrosion on transportation and solar energy technologies with emphasis on road transportation. The impact of corrosion on other sectors of our economy and on other technologies is dealt with on a case-by-case basis elsewhere in this report.

The remainder of this report addresses the needs and opportunities for improved corrosion protection in transportation and solar utilities systems. The emphasis will be given to surface modification and surface characterization because recent advances have provided a basis to propose that marked advances will be realized in the near future by focused efforts in both. Many of the modification techniques, such as overcoating with a metal or an organic layer or film, are highly developed and mature, while other high energy deposition techniques are still being developed. The characterization efforts support surface modification in two general ways: first, failure of films or coatings may be caused by interfacial processes, either mechanical or chemical. Analysis of defects, both the scale and the type, and analysis of surfaces help to identify the degradation processes; second, characterization of surfaces and interfaces provides a foundation on which to base new or improved modification techniques. Because the interface of a reactive metal or semiconductor oxide film is usually buried beneath the protective overlayer, study of that interface presents special problems.

The survey of surface modification and characterization will be preceded by illustrative systems that are near success and by a system in which long-range efforts are required. And finally, a list of specific recommendations will be given for future work in corrosion protection.

II. IMPACT OF CORROSION CONTROL BY SURFACE MODIFICATION AND CHARACTERIZATION

The prevention of corrosion by surface processing enjoys significant economic leverage, and as evidence, one may cite the widespread use of coatings, films, and inhibitors for metals and semiconductors in many service environments. Corrosion control contributes to the vitality of existing and developing technologies in automobiles and in solar energy systems. The successful implementation of existing surface modification methods has greatly reduced the effects of corrosion in automobiles over the past decade, in response to consumer demand. The application of available corrosion control methods has also been effective in solar thermal and solar photovoltaic systems. Nevertheless, significant problems remain because of the limitations of existing control techniques, or because increased lifetimes are desired. Because incremental improvements in these and similar engineering systems will ensure their economic viability, they are considered to be over the threshold establishing feasibility. Discussion of those areas in which progress has been made calls attention to both the strength of present technologies and the need for long-term corrosion research based on a systematic and comprehensive approach.

As expected, these successful corrosion control methodologies have focused on three main issues of surface modification:

- Improved quality control to minimize defects
- Improved materials selection to reduce susceptibility
- Development of more advanced, tougher, and more durable coatings and films.

In addition, improved design can contribute to improved corrosion resistance.

In the following examples, the surface modification techniques discussed are metal overcoats, which provide galvanic protection for automobile body panels, and polymeric encapsulants for solar mirrors and photovoltaic systems. In both cases, the essential protection processes are known, i.e., "active" galvanic protection of the iron substrate by a sacrificial zinc overcoat for automobiles and by a polymer barrier layer to reduce the penetration rate of aggressive species from the environment into solar collection devices. Even though the modifications are understood, and indeed they have been used effectively, modest improvements would have large economic benefits. Thus, improved materials, improved surface processing, and improved understanding of the corrosion systems are needed.

A. Corrosion in Road Transportation Systems

Automobiles are complex systems composed of structural components, a power plant, a drive train, electronic controls, and features for passenger comfort. Failure mechanisms in automobiles include corrosion, wear, fatigue, and combinations of all these processes. When new materials are introduced, the failure mechanisms change as well. At present, for example, lighter, stronger materials are entering vehicle design to reduce weight and thus to improve fuel economy. As U.S. automobile manufacturers use more of these lightweight materials, the basis for understanding those factors that determine durability and those that lead to failure must be improved.

Today's vehicle is based on steel, with significant fractions of aluminum alloys, magnesium alloys, and polymers. Structural and body panel materials must resist road damage and corrosion from salt and acid rain. These components are now protected with sacrificial coatings, with conversion coatings, and by paint. Material for the fluid control and power train components must withstand wear and corrosion when in contact with coolant, refrigerant, fuel, oil, and transmission fluid. Couplings of different materials must be managed carefully to avoid galvanic couples, which induce corrosion.

American automotive manufacturers have introduced zinc-coated steel throughout the vehicle as the major protection system against salt-induced corrosion. The material is roll-coated by the steel manufacturer, using either hot-dip or electrodeposition processes. At present, American manufacturers use pure zinc coatings for the outer body panels, but advanced hot-dip coatings are now being accepted. Zinc-based coatings are sacrificial to the body steel and prevent iron corrosion when the paint layers are damaged. Japanese and European manufacturers also use zinc or zinc alloy coatings. The Japanese have established a leadership position by developing a large number of binary alloys at the production scale. Two factors are presently driving a search for replacement sacrificial coatings:

(1) Zinc is highly active electrochemically and corrodes without coupling. Alloying is considered a route to longer-lived coatings by reducing the self-corrosion of zinc, thus extending the life of zinc. A second goal may be to reduce the zinc-iron galvanic current to the minimum required for acceptable protection of the iron. It is desirable to estimate the size of an iron surface (exposed, for example, through a hole in the protective overplate) that may be cathodically protected by the nearby zinc or zinc alloy.

(2) Pure zinc coatings weld poorly, cause paint adhesion problems, and powder or gall in stamping dies. Selected alloy coatings have fewer manufacturing problems and are cheaper to process, but it has yet to be established that the alloys have adequate corrosion resistance.

A recent paper has noted the need for scientific understanding of the interaction of such alloys with saline corrosive environments to improve the selection of materials and the design of superior coatings [2].

A new set of needs is also emerging as automotive manufacturers move to reduce weight by substituting polymers and light metals for steel and by moving to lower-mass designs. Both aluminum and magnesium alloys are completely recyclable, and there are processes under development that could reduce the production cost of magnesium, in particular. Aluminum alloys are already used extensively—for wheels, trim, air conditioners, and drive train components—and magnesium alloys are growing in acceptance. For the present applications, corrosion is manageable by anodizing or conversion-coating the metals and striving to remove galvanic couples in the vehicle. However, as the light metals become used more in functional parts of the vehicle—notably in the drive train—and as the thickness of the alloy drops for weight reduction, the need for robust corrosion prevention grows. Technical issues include (1) understanding and tailoring the aluminum (and magnesium) passive layer for alloys,

(2) identifying factors that control the corrosion of light metal alloys, and (3) using accelerated tests to assess the corrosion rate of light metals in automotive applications.

Vehicles are manufactured by a series of forming, joining, and coating operations. After assembly, vehicle bodies are first coated with a chemical phosphate conversion layer that improves final corrosion resistance and anchors the paint. Industrial phosphate conversion coatings are based on the reaction of the metal substrate with phosphate anions to facilitate the precipitation of phosphate crystals [3]. The reaction is heterogeneous with distributed anodic and cathodic areas. As soon as 95%-99% of the surface is covered with phosphate, the active deposition of phosphate stops, and portions of the metal surface remain uncoated. Those parts of the surface that are not coated will be unprotected and also may not bond well with the overcoats. Chromates and inhibitors have been used to provide temporary protection to the uncoated areas. It is desirable to have a process that will provide complete coverage. After phosphate treatment, bodies are electrophoretically painted in an immersion tank. After the primer step, the coating is completed with spray-on color and protective layers. Aluminum components, such as air conditioners and wheels, are either anodized and painted or conversion-coated to resist corrosion.

A quantitative assessment of the quality of manufacturing processes and the evolution of corrosion damage requires the use of monitors that are sensitive and accurate and provide an output that can be related to a component dimension and the geometry of the damage (e.g., general attack versus pitting). Monitors are also required to assess the quality of painting, formation of phosphate conversion coatings, and electrophoretic deposition of primers. The monitors should operate in "real time," so that the output is available as the manufacturing process proceeds. The development of effective monitors for quality assurance is a critical issue in any highly competitive manufacturing activity (such as the automobile industry), in which economy of scale depends on uninterrupted throughput.

An area of particular concern in the automobile industry is the development of quality assurance monitors for the phosphate conversion and electrophoretic coatings. Because researchers desire to monitor in "real time" and to have minimal impact on the manufacturing activity, the desired monitors should be remote and hence should use optical or electrical techniques where possible. The optical monitors may use absorption, scattering, or fluorescence phenomena at closely specified excitation frequencies employing tunable lasers and narrow band sensors. Neural networks and expert systems might be employed to provide a diagnostic capability, so that the manufacturing and processing parameters may be closely controlled for optimal performance.

Because of the extremes in pressure (force) and temperature experienced by components in modern high-performance engines and drive trains, a need exists to develop reliable sensors for corrosion and wear. Examples of such sensors include monitors for coolant corrosion and corrosivity, engine wear, oil lubricity, transmission fluid viability, etc. The outputs of such sensors would provide data to a central, on-board computer that in turn would provide continuous diagnostics of the mechanical and tribometric state of the engine and drive train, so that the vehicle may be operated in the most efficient manner possible.

An on-line sensor for engine wear and corrosion is a short-term possibility, because crude sensors of this type already exist in the aircraft industry. This sensor would provide "real-time" measurements of wear and corrosion of critical engine and drive train components and might become the basis for scheduling the maintenance and replacement of these components. Because of the high sensitivity of radioactive isotope detection, radionuclear techniques would seem to be promising.

Sensors are also required to monitor corrosion inhibitor levels and oil breakdown products in high-performance engines and drive trains. Again, "real-time" monitoring and diagnosis are desired, with both an output and memory that are available for system servicing.

Sensors for coolant viability appear to be a relatively near-term possibility. These sensors might monitor pH and the buildup of degradation products, with particular emphasis on adjusting coolant flow for optimum engine performance. Because the generation of acidic breakdown products is of major concern, the pH might be a parameter of great importance.

Finally, with regards to the emerging needs for improved corrosion protection, it should be noted that there is renewed worldwide interest in the electric vehicle (EV). This interest has kindled active development of batteries and fuel cells that are capable of high energy and power densities and that exhibit long cycle lives. In these power plants, the energy is stored and delivered by electrochemical reactions. Corrosion is a principal cause for EV power plant degradation, and the mechanism of corrosion in these systems is often electrochemical. The first EVs most likely will be powered by advanced <u>lead-acid</u> batteries, which have high power densities, moderate energy densities, and long cycle life. The positive grid is a nonequilibrium system, and progressive grid oxidation decreases capacity. Conductive diluents, such as carbon, for the active lead dioxide improve life, but they commonly oxidize too rapidly to be practical. Corrosion of the metal negative grid is an undesirable corrosion reaction that also reduces battery life. <u>Metal hydride</u> batteries—typically including the nickel/nickel oxide positive—are a strong contender for the second-generation EV battery. Corrosion of the hydride-forming electrode material is a problem, because the formation of any oxide passivates the system and reduces performance. The nickel positive electrode requires a nonpassivating grid surface, crucial when the lower-cost nonsintered construction is used. Cost-effective surface modification routes to a nonpassivating nickel electrode could increase the nickel-metal hydride battery performance to a level matching EV requirements. In the elevated temperature <u>sodium-sulfur</u> battery, a major problem has been to maintain a seal between the beta-alumina separator and the reactants, sodium and sulfur. Corrosion in the <u>lithium solid polymer electrolyte</u> battery and in <u>polymer electrolyte fuel cells</u> has a significant impact on performance, because the electrolyte is immobilized, and corrosion products formed at an electrode-polymer interface are not easily removed or circumvented. Lithium solid polymer electrolyte batteries are among the most promising EV power sources over the long term.

Mechanisms by which electrochemical energy conversion systems degrade are complex and take place on a small scale, typically occurring at interfaces. The combination of powerful, sophisticated vacuum spectroscopies with microscopy techniques used in corrosion science can identify these mechanisms from the reaction products and, thereby, lead to appropriate alternative material combinations. Electrochemical impedance analysis has the ability to probe a battery or fuel cell during operation to follow degradation processes as they occur. Finally, the current/potential models of corrosion science are directly applicable for identifying system instabilities and for guiding battery/fuel cell designers in minimizing harmful reactions.

B. Solar Energy Systems

A capacity of over 50 MW of a photovoltaic (PV) electric power has been installed in the United States. The lifetime of the PV modules appears to be on the order of 10-15 years. For solar PV power to be economically viable, the power packages must have a useful life of 30 years. Likewise for solar PV concentrator power packages, and for solar thermal heat and power generation, the lifetime of the parabolic mirrors is a critical limiting factor in the longevity and reliability of the power system. Second-surface mirrors are used so that the surface can be periodically cleaned. The most common mirror consists of glass/Ag/Cu/paint and polymethylmethacrylate (PMMA)/Ag/adhesive/Al. The latter is more desirable, because it is flexible and much lighter in weight and hence requires a less massive support structure.

A requirement of both mirrors and solar cells is that they be fabricated from inexpensive materials, because future markets indicate that many square miles of solar cell arrays will be manufactured, and the cost/kWh must be kept as low as possible to compete with fossil fuels and nuclear power. For this reason, the lightweight mirror mentioned above has an inexpensive PMMA protective coating over the Ag. Over a period of time, the PMMA either reacts with the Ag, or impurities and H_2O penetrate the PMMA and cause the Ag to turn black and to roughen. The exact degradation mechanism is not known. The corrosion problem limits the lifetime of these inexpensive mirrors.

Flat-plate photovoltaic modules are distinguished by the photon absorber, such as single-crystal silicon (c-Si), polycrystalline silicon (p-Si), amorphous Si (a-Si), copper-indium-diselenide (CIS), or cadmium-telluride (CdTe). The solar conversion efficiencies are approximately 14% for c-Si, 12% for p-Si, and less than 10% for a-Si, CIS, and CdTe. Most flat-plate modules have Ag or Al contact grids or films that need corrosion protection from moisture. The lifetime needs to be 20-30 years. For photovoltaics to be cost-effective for terrestrial applications, low-cost pottants are needed over areas up to 2 m^2. The terrestrial and space-qualified c-Si modules are similar in design. However, in order to reduce the cost, lower cost materials have been substituted in the terrestrial modules. The module structure is glass (substituted for fused quartz)/ethylene-vinyl-acetate pottant (substituted for silicones)/Ag or Al contacts (substituted for Pd/Ag)/Si cell. The problem with this cell is ultraviolet (UV) degradation of the pottant and subsequent reaction with the contact materials by the degradation products; this limits the useful lifetime of the photovoltaic modules.

Electrochromic materials have optical absorption properties that may be changed on demand by an externally applied potential. Many of the materials respond to insertion or intercalation of ions from a contiguous electrolyte, and on release of the inserted species, the optical properties are switched back to those of the starting material. The basic phenomena can be used for a variety of technologically important solar applications, such as light modulation or reflectance. The reversibility of the switching process is essential, and the stability of the electrochromic character has emerged as a key factor that limits the use of the present systems. Many of the promising materials are transition metal oxides that are hosts for cation (e.g., H^+, Li^+) guest species. "Smart windows" for homes or offices and "smart mirrors" for automobiles have been demonstrated and installed in consumer products on a limited basis. The general outlines of the process are reasonably well understood, and further work to enhance the cycle life of the materials will support a more widespread use. A recent symposium has described the progress in research on the materials and their use in a variety of electrochromic devices [4].

III. SURFACE MODIFICATION TECHNIQUES

The improvement of corrosion resistance of metals by modification of the surface has been practiced since the invention of metal tools. All engineering metals used in today's technological societies are unstable with respect to corrosion, which causes the loss of properties. Natural oxide films provide protection against continued attack for some metals, and alloying extends the life of other metals by developing highly stable passive films. Metals may not always be protected by oxide films, and other modification methods have been developed. Some of the earliest techniques to prevent corrosion involved coating with greases or natural oils. More modern methods developed in the 19th and 20th centuries include multiple coatings (the most common of which are paints and polymer films), Zn galvanizing (sacrificial coatings), electro- and electroless plating of other pure metals, and vacuum physical vapor deposition of mostly pure metal coatings by electron beam, and radio frequency (RF) and direct current (DC) magnetron sputtering. The metal coatings are better barriers than the organic films because of the lower permeability of the former to moisture and oxygen. Inhibitors or conversion coatings as primers for paints are also used by paint manufacturers, and they remain, even today, highly proprietary in nature.

The use of organic coatings to protect metal surfaces is widely practiced. Much of the use is for atmospheric exposure of vehicles as well as for structural units such as bridges and buildings. The technology of such coatings has advanced significantly in the past few decades. Automobile coating systems have been developed that, under favorable conditions, last the lifetime of the vehicle. However, coating technologists and coating scientists acknowledge that much is unknown and that new processes and understanding are the keys for further progress [3]. Defects in the metal substrate and in the overlayers are among the primary concerns, because they are the source of localized corrosion phenomena. Defects may occur on length scales from atomic level lattice vacancies to arrays of defects at grain boundaries (for crystalline materials), or to random pores or cracks (for example in noncrystalline films). Avoiding such defects by proper quality control is a major concern in coatings science and technology.

In the past 15-20 years, an explosion of interest in surface modification techniques has mostly involved depositing thin films, applying coatings, and forming surface alloys. The development of many of the techniques has been driven by the need for the semiconductor electronics industry to create improved processing procedures. As a spin-off of the advancing technology, other fields, such as corrosion protection, can benefit from the new processes.

It is not the purpose here to explain each of the new processes in detail, but some familiarity with them will be assumed. As an aid to further discussion in this section, however, Tables 1 and 2 are provided as a compilation of surface modification techniques. The list is not all-inclusive, but is intended chiefly to highlight advanced methods that may have application to corrosion protection. The techniques of surface modification are divided into three broad categories:

- Low energy inorganic coating techniques. For the most part, these are mature technologies that have been used for many years. Table 1 summarizes factors pertaining to the use of these techniques.

- Techniques involving the use of energetic ions. These techniques have largely appeared within the last 10-15 years; several have neither reached maturity nor found use for corrosion protection. Higher densities and better adhesion of the coatings are among the commonly accepted advantages of these techniques. Table 2 summarizes the relative features of the energetic techniques.

- Polymer coatings include traditional paints, thermoplastics, polyvinylchlorides, epoxies, urethanes, and polymethylmethacrylate.

Because many of the techniques for corrosion protection in the automobile industry must be low cost and scaled up to large areas and high volume, only those techniques in the tables that are designated as low cost and highly scalable are viable, although future advances in the other techniques could place them in a viable category. In addition, most techniques that involve vacuum processing are too costly for automotive applications. For solar energy problems, vacuum deposition is already used in processing steps so that many of the vacuum deposition techniques may be applied without cost penalties.

A. High Energy Surface Modifications

High energy surface modification processes currently find their widest use in the electronics industry. Ion implantation, for example, is used in all economically advanced countries for controlled doping of components of integrated circuits. In part because of this success, research is now directed toward surface modification for other purposes, including corrosion protection to preserve the useful

Table 1. Low Energy Inorganic Coating Techniques

#	Technique	Ref	Cost	Thickness (microns)	Throwing Power	Area/ Scalability	Wet/Dry	Environmental Impact
1	Oxide passivation		Low	1	Yes	Yes	Wet	High
2	Electroplating	(i)	Low	1 to 10	No	Yes	Wet	High
3	Electroless metallizing	(i)	Low	1 to 5	Yes	Yes	Wet	High
4	Galvanizing		Low	1 to 10	Yes	Yes	Wet	Low
5	Conversion coatings (silicates, phosphates)		Low	1	Yes	Yes	Wet	Low
6	Physical vapor deposition (PVD)	(ii)	Low	1 to 20	No	Yes	Dry	Low
7	Chemical vapor deposition (CVD)	(ii)	Med	1 to 10	Yes	Yes	Dry	Low
8	Laser assisted CVD (LACVD)		Med	1 to 10	Yes	Yes	Dry	Low
9	Sol-gel	(iii)	Low		Yes	Yes	Wet	Med
10	Plasma spraying		Med	+400	No	Yes	Dry	High

(i) See Chapter 10, this volume
(ii) See Chapters 12 and 13, this volume
(iii) See Chapter 14, this volume.

Table 2. Coatings Techniques Involving Energetic Ions
(All are performed in vacuum and provide for low substrate temperature.)

#	Technique	Ref	Approx. Energy/Atom	Cost	Thickness (Microns)	Throwing Power	Dry/ Vacuum	Area/ Scalability	Comments, Special Suitabilities
1	Sputtering (magnetron)	A	10 eV	Med	1 to 20	Yes	Yes	High	In wide use
	Ion beam sputtering		10 eV			No		Med	Excellent control
	Biased sputtering		100 eV			Yes		Med	Highest energy
2	Pulsed laser deposition (PLD)	B	10 eV	Med	1 to 10	No	Yes	Low	Epitaxy, complex materials
3	Plasma assisted CVD (PACVD)	G	10 eV	Med	1 to 25	Yes	Yes	High	Wear/corrosion coatings
4	Ion plating	A	10 eV-100 eV	Med	1 to 10	Yes	Yes	Med	Wear/corrosion coatings
5	Ion cluster beam (ICB)	C	10 eV-100 eV	Med	0.1 to 6	Yes	Yes	Med	Mirrors, epitaxy, controllability of energy, no co-ions
6	Ion beam deposition (IBD)	D	10 eV-100 eV	High	0.1 to 1	No	Yes	Low	Epitaxy, DLC compound semiconductors
7	Ion beam CVD (IBCVD)	G	100 eV-1 keV	Med	1 to 100	No	Yes	High	DLC, new technology
8	Ion beam assisted deposition (IBAD)	E	100 eV-20 keV	Med	1 to 20	No	Yes	Med	Control/graded composition/ microstructure
9	Ion implantation	F	100 keV-400 keV	Med/ high	0.1 to 1.0	No	Yes	Med	High flexibility for all types of substrates

Table 2. Coatings Techniques Involving Energetic Ions (Concluded)

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properties of substrate materials. Research and applications in the area of wear resistant and corrosion resistant coatings for metals by means of several of the energetic deposition techniques listed in Table 2 are just beginning. Others are quite mature.

Because films deposited using energetic deposition techniques are dense, highly adherent, have few pin-holes, and can be laid down at extremely low temperatures, they are attractive for corrosion protection applications. It could be said that with the results of research already conducted, that corrosion problems involving planar and cylindrical geometries can already be solved using dry energetic deposition techniques. The problem then reduces to which technique to use, and how one can reduce the cost by scale-up of processing. Ion beam assisted deposition and ion implantation have the best adhesion properties, while RF sputtering has the best throwing power, so which one to use will probably be decided by the specific application.

From the historical standpoint, many of the techniques identified in Table 2 have some connection either to the ion plating technique invented by Mattox [5] or to the high energy ion beam implantation technique [6]. The latter technique came into wide use in the 1970s for the carefully controlled introduction of dopants into elements of integrated circuits. The ready availability of processing equipment and the general scope of the enterprise helped stimulate research into the use of high energy ion beams for surface engineering of all types, including corrosion, wear, optical, and conducting properties. The advantages of high energy processing soon became apparent. Direct implantation has the disadvantage of rather low throwing power, however. Therefore hybridization of beam techniques with other deposition processes to achieve high energy deposition together with more mass deposition has occurred. Meanwhile, for the plasma techniques, microwave plasma generation and RF plasma generation have come into wider use.

As has been pointed out [7], three important factors affecting the performance of films and coatings are porosity, adhesion, and stress. Direct high energy ion implantation may have some advantages in all three categories for pure corrosion protection. This assumes that the surface alloy formed by ion implantation itself has suitable corrosion resistance and that externally applied mechanical stresses associated with the application are not severe enough to damage the thin treated surface. Although there are compressive stresses in ion implanted surfaces due to added atoms, delamination by buckling is practically unknown. It might seem that effective porosity (weakness in the treated layer) could exist due to shadowing of the surface from the beam by contaminating particles. Thus far this problem does not appear to have been identified, but the exact reason is not known. Porosity remains something of an issue for pure corrosion protection by the other techniques as well [7]. A possible attractive application for direct ion implantation is in the area of fretting corrosion, in which even energetically deposited coatings might fracture and spall due to the repeated vibratory impacts.

With the exception of ion implantation, only a few studies on corrosion have been done on films deposited using energetic deposition methods. The early results look promising. Wolf [8] has studied ion beam assisted deposition (IBAD) Pt, TiC, TiN, B, DLC, CrN, BN, Cr_2O_3, and Si on metals with good success, and others have studied Al, Ta, and W on carbon steel. Carbon steel is cheap and workable, and IBAD films have good adhesion and high corrosion resistance. Thus, even though the process may be expensive, use of inexpensive substrate materials can obviate some of the processing cost.

Ceramic compound films such as Al_2O_3 and Si_3N_4 and TiN also offer excellent corrosion resistance. Takahashi in Japan has set up a processing line which coats steel sheet continuously with Al, TiN or Al_2O_3 [9]. His system provides for sputter cleaning, evaporative coating or CVD coating in series in one vacuum process line. Part of the success of IBAD films is that they are adherent and more ductile than bulk materials due to the microcrystalline or amorphous structures. Therefore, they can yield along with the metal sheet so that some working of the metal is possible after application of the coating.

Many of the applications described above require large areas to be coated. Ion guns more than 60-cm long are currently available, and at least one laboratory has a system that can handle 1-m-diameter workplaces. In nonoptical applications, in which uniformity of the film is not a strict requirement, very large areas could be coated with present equipment by routine manipulation of the workplaces.

Still higher surface areas are possible by the means of continuous coating of rolls inside vacuum as mentioned above. The primary obstacle for scale-up is the requirement of line-of-sight processing, especially for odd-shaped parts. Cylinders can easily be coated, but it is not yet clear whether shapes like gear teeth can be reliably coated.

Electrodeposition is very inexpensive but may be phased out where there is a severe environmental impact of waste products associated with the process. Dry processing with techniques such as physical vapor deposition (PVD) are inexpensive but suffer from poor adhesion and low-density films. Chemical vapor deposition (CVD) films are very attractive when the pieces to be coated can be heated to high temperature, and this process will probably always win against energetic processes. However, adhesion is often a problem with the CVD technique. When the substrate requires a low deposition temperature, when perfect adhesion and no pin-holes are required (as it is when a material of low thermodynamic stability is to be coated), then energetic deposition methods are a viable choice.

Costs are difficult to determine because only the work by Takahashi [9] has attempted to scale-up these processes to large area sheets. A useful comparison is the cost of magnetic tape or coatings for Lo E windows, which are both made by PVD or sputtering techniques. Energetic deposition processes will be somewhat more expensive than the other processes for coatings of magnetic tape or windows. The cost should be in the area of \$1-\$15/ft^2.

B. Protective Layers of Zinc

Zinc coating is a surface modification technique that has a substantial history, several aspects of which have created renewed interest. In the last 5 or 6 years, essentially all steel components of vehicles sold in the United States have been zinc coated. The improvements in corrosion protection have been dramatic, but the costs have also been substantial (~ \$1 billion/year). The principle of galvanic protection with sacrificial zinc coatings is well established, because it has been discussed in textbooks [10-13] and in the specialist literature. Galvanic interactions have also received attention from mathematical modeling [14-18] including situations that simulate atmospheric exposure [19,20]. A more complete understanding of the role of alloying, microstructure and microcomposition, phosphate plating, and electrophoretic primers and paints in corrosion protection would permit improved design of the zinc layer with significant cost savings.

C. Surface Modification by Sol-Gel Films

A general discussion of sol-gel film technology is given in Chapter 14 of this volume. Broadly speaking, a sol-gel film is a coating or free-standing film that is formed from a sol through continuous stages of increasing concentration of a solid precursor. Typically, the sol is a solution of polymeric species or a suspension of "oligomers" including, possibly, particles in the colloidal size range. During deposition through states of increasing solids concentration, this sol might gel, as in bulk sol-gel processing; however, the gel state is often a fleeting transient that quickly empties of liquid. Nevertheless, the structures formed during this stage, with varying amounts of porosity, influence the structure of the final film.

Sol-gel processing offers high compositional and homogeneity control at low temperatures. In comparison with vacuum and CVD techniques, sol-gel coating is not equipment-intensive or directional. Complex shapes of arbitrary size can be coated with reasonably good uniformity. Single-coat thicknesses depend strongly on sol concentration and fabrication technique; for dip and spin coating, 200 nm is a typical (but not unsurpassable) upper limit, and 5 nm is a typical lower limit. Multiple coats are feasible, generally requiring thermal treatment between coats in the absence of well-matched thermal expansion coefficients. The cost of high-purity liquid precursors can be high, but in thin-film applications, the materials cost would normally be negligible.

Commercial sols are available for protective coatings that offer both corrosion and abrasion resistance. "C Resin" from Dow Corning Corporation is a sol-gel that contains fumed silica particles for strength and wear resistance. A similar siloxane-based product, "H Resin," is available for corrosion protection of microcircuitry [21]; it has the distinct sol-gel advantage of low-temperature (down to 175°C) application. Tests have demonstrated its effectiveness in preventing salt-water attack.

D. Nonchromate Alternatives to Alodine Conversion Coatings

Most schemes for the corrosion protection of aluminum are based on highly toxic hexavalent chromium; "alodine" is a proprietary chromate-based conversion coating used widely in the aircraft industry. Applied by dipping or spraying, alodine imparts superior corrosion resistance to aluminum with an added bonus: scratches heal themselves. Apparently the migration of chromium into scratches inhibits corrosion. In addition, for some applications, the relatively high conductivity of alodine can be exploited (e.g., the RF shielding effectiveness of aluminum casings).

Unfortunately, chromate is toxic, and it may be eliminated by future mandate. Therefore, alternatives to chromate conversion coatings are in high demand, as are protective coatings for all light metals in general. Although polymeric coatings are under study, the ideal replacement must resist UV degradation to satisfy aircraft requirements.

IV. SURFACE CHARACTERIZATION TECHNIQUES

Surface characterization techniques have been used for corrosion studies over wide length scales from the detection of damaging surface species (like chloride or sulfur) to the location of defects in protective films. The use of such methods has become more sophisticated as their capabilities have been enhanced, especially their sensitivity to surface and near-surface regions of reactive metals and semiconductors. For the purposes of the discussion here, these methods may be categorized as either ex situ, meaning characterization of the surface in vacuum or out of the working environment, or in situ when referring to analysis in the environment. In the latter category, we include techniques that can be used to interrogate "buried" interfaces below protective films that remain in place. The shift in emphasis to in situ techniques has been based on recent advances, and we anticipate that this will accelerate in the future.

Monitors or sensors that operate on devices in use, in factories, on operating solar devices, or on working vehicles form a third category of engineering characterization technology relevant to corrosion science. Many of these monitors are based on in situ surface characterization techniques.

Practically all of the vacuum ex situ techniques have been reviewed in Chapter 1 of this volume. They include Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion scattering spectroscopy (SIMS) secondary neutral mass spectrometry (SNMS), ion scattering spectroscopy (ISS) and Rutherford back scattering spectroscopy (RBS). Many of these are useful for characterization of passivation layers and other interfaces subject to corrosion.

Particularly for systems subject to aqueous corrosion (of primary interest here), the ex situ techniques have the disadvantages that removal of the sample into vacuum may have uncontrolled effects on the surface and that the corrosion processes cannot be monitored in real time. In situ techniques avoid these problems. Recent developments include environmental scanning electron microscopy in which electron microscopic images are obtained in ambient pressures up to 10 Torr of arbitrary gases, including highly reactive species such as HCl, H_2O, and SO_2. We will discuss the in situ techniques in some detail because they are especially promising for new corrosion studies.

A. Tunneling and Atomic Force Microscopy

A tremendous advantage of these methods is that they permit angstrom-scale images in aqueous environments. A disadvantage is that, until recently, it has been impossible to distinguish one atomic species from another in the images; this distinction may soon become possible through the use of a scanning tunneling spectroscopy (STS), in which the conductance of the interface is studied as a function of tip position.

If a relation can be established between the local density of states and the species over which the tip is suspended, then the needed identification can be made. Theoretical calculation of the local density of states as well as a better theoretical characterization of the tunneling process itself have a role to play in putting this advance on firm ground. Recent papers by Chidsey [22] and by Snyder and White [23] have discussed recent progress on studies of reactive surfaces.

B. Grazing Incidence X-ray Diffraction

X-ray probes are the primary direct tool for structural analysis of materials, including oxides. Until recently, only indirect structural probes were used to study anodic oxide films whereby the structure was inferred on the basis of some physical property such as capacitance, photoelectrochemistry, or spectroscopy. Very few direct structural measurements were reported, and these were dominated by electron scattering. This limitation has been overcome through the use of grazing-incidence X-ray scattering using synchrotron light sources. A recent review of surface X-ray studies summarizes the recent progress at electrochemical interfaces [24]. By variation of the angle of incidence, one can probe, in turn, the upper interface, the bulk, and the buried lower interface of a thin film. The technique is sensitive to monolayers. The first application of this technique to an anodic film of TiO_2 was reported recently [25,26]. Studies have begun to appear for other systems as well [25].

C. Extended X-ray Fine Structure Spectroscopy (EXAFS)

Although not an inherently surface-sensitive technique, EXAFS can be useful for surface studies if the interface is labeled with a species not present in the solution or the substrate metal. Surface studies with EXAFS and surface extended X-ray fine structure spectroscopy (SEXAFS) have been reviewed in Chapter 7 of this volume. This labeling can be done by underpotential deposition as in the work of Melroy et al. (see [24] and references therein). The characterization of passivation layers has been carried out by J. Kruger, G. Long, and coworkers [28], by Froment et al. [29], and by O'Grady and coworkers at NRL [30]. EXAFS spectra are sometimes difficult to interpret as a consequence of ambiguities in attempts to fit existing theoretical models for the absorption spectra, and this aspect requires theoretical attention. EXAFS provides information on local coordination number and neighbor distances. It can be used for surfaces and for buried interfaces.

D. Neutron Reflectometry

Although X-ray reflectometry has been a standard, if not widespread, surface characterization tool for some time, its counterpart using neutrons is relatively unknown. (The recent dearth of neutron sources in the United States has stunted growth in this area.) Nevertheless, certain advantages for neutron reflectometry for studying "buried interfaces" should be brought to the attention of the corrosion community.

Neutrons will reflect specularly from a smooth interface with high efficiency when near the critical angle (glancing a few degrees from the surface). Two interfaces create a characteristic interference pattern that can be used to measure layer thickness; density variations within the layer (normal to the substrate) can be determined from the interference signature. Most important to corrosion problems, perhaps, is the diffuse scattering parallel to the surface around the specular reflection, because it contains information about in-plane variations on the interface.

The key advantage for neutron experiments vis-a-vis X-rays is penetrability. Metal overlayers that stop X-rays present no special impediment to neutrons. Because the scattering length density is, roughly speaking, a random function of atomic number z, isotopic labeling is often useful. Spatial resolution for neutron reflectometry is typical of small-angle scattering: 1 to 100 nm. National user facilities have been established for neutron reflectometry at LANSE (Los Alamos) and the National Institute of Standards and Technology (NIST).

E. Electrochemical Impedance Analysis

Variable frequency techniques to characterize reactive interfaces are mature and continue to expand. Reaction rates at interfaces, the deposition and growth of corrosion product films, and the evaluation of coatings (e.g., permeability, defects and pores, film delamination, and heterogeneous pathways for ionic species) are addressed by impedance measurements (MacDonald [31] has a recent review of such applications, as does Mansfeld and Bertocci [32]). Localized scanning methods have appeared recently (see Lillard, et al., [33]), but their use is not widespread. There are also international symposia in which impedance analysis is discussed, including results for corrosion systems (The Second International Symposium on Electrochemical Impedance Spectroscopy will be held in 1992 in the United States). For simple systems, the use of impedance is straightforward, but more complex, heterogeneous surfaces have multiple processes that occur simultaneously. In the latter case, the measurements must be used in conjunction with theoretical models based on the fundamental processes taking place at the interfaces. Fortunately, such modeling for the interpretation of experiments has begun to appear (e.g., the work of Newman [34] and references therein).

F. Spectroscopic Ellipsometry

Although this is not a new method, it has been insufficiently used for characterizing the electronic structure of the passivation layer in corrosion studies. A major reason has been the difficulty in interpreting the rather complex spectra. Recent advances in the calculation of optical conductivities of microscopic models of highly disordered oxides have begun to make these interpretations feasible [35,36]. The extension to the study of the interface between the substrate metal and the protective overlayer is one of its most promising features.

G. Imaging Ellipsometry

Problems in microcircuit fabrication, wetting, and coating have driven the recent development of ellipsometers capable of imaging (e.g., Streinz, et al. [37]). Based on standard photometric ellipsometers, imaging systems have been incorporated covering a range of transverse spatial resolutions from 1 to 5 μm at the low end to fields as large as 2 cm, depending on the problem of interest. In general, spatial maps of film thickness and index can be obtained at a given wavelength, although, in principle, multiple wavelengths could be used. The main difference between imaging ellipsometers and conventional ellipsometers that scan the sample point by point is the ability to capture time-dependent phenomena over a wide field of view.

H. Phase Detection Interferometric Microscopy (PDIM)

PDIM is rapid, versatile, and more accurate than traditional interferometric microscopy. Instruments are available that have a vertical resolution of 0.2 nm and a larger lateral resolution of ~ 0.5 μm. PDIM has been used for topographical imaging of reactive surfaces (White et al. [38]) and for thickness and refractive index measurements of solvent swollen films (Smith et al. [39]). The instrument has a demonstrated capability of monitoring changes of morphology of a buried interface beneath an aqueous solution or polymer film; it may also be used to measure film detachment or deadhesion.

I. Infrared and Raman Methods

Infrared methods that are partly surface-specific have begun to be used, although they require very good surfaces. Surface enhanced Raman scattering (SERS) remains difficult to interpret due to problems in quantitatively characterizing the various enhancement mechanisms. Spectroscopic techniques for surface studies have been reviewed in Chapter 3 of this volume.

J. Second Harmonic Generation (SHG)

SHG is a useful in situ optical method and has been discussed in Chapters 4 and 5 of this volume. A general difficulty is that theory seriously lags behind experiment in its ability to quantitatively predict spectra, given a microscopic model. This means that only qualitative interpretations are possible at present. Theoretical efforts to account for the effects of the aqueous (or other solvent) environment are in a preliminary stage.

K. Optical Fiber Probes and Near Field Microscopy

Optical fibers have proved to be a versatile and valuable tool for investigations that range from spectroscopic probes to physical optics. Further, they are the basis for developments of several sensor systems. In the latter field, Butler and colleagues [40-41] have used optical fibers to study chemical interactions of metals with gaseous environments, and the extension to liquid systems is straightforward. Moreover, Betzig et al. [42] have fabricated microfibers to obtain optical spatial resolutions of the order of l/50, far below the diffraction limit. The use of such techniques to perform super resolution microscopy on reacting surfaces in situ could give useful information.

L. Quartz Crystal Microbalance (QCM) Gravimetry

The QCM has been used extensively in gas and vacuum systems for monitoring film thickness changes [43]. Single layers of inhibitors, self-assembled monolayers, Langmuir-Blodgett films, or corrosion product films could, in principle, be detected because the QCM is sensitive to fractions of an atomic layer. Corrosion of several metals has been investigated in gaseous or humid ambient environments, as well as in liquid solutions. When associated with electrochemical and spectroscopic measurements, surface degradation processes of some complexity can be characterized. Recent reviews are available for corrosion applications of the QCM, including atmospheric exposure [44,45].

M. Modeling

Successful surface characterization depends in many cases on successful modeling of the interface being characterized in order that the experimental output of the measuring instrument can be meaningfully interpreted. As examples, we have mentioned the model dependent interpretation of SEXAFS, SERS, STS, and ellipsometry above. Generally, modeling capability has increased significantly in the recent past as a consequence of dramatically improved computing capability as well as the introduction of various simulation techniques (molecular dynamics, Monte Carlo, equation of motion, Car-Parinello methods and others) to electrochemical and corrosion problems.

Corrosion systems consist of complex interconnected and interrelated components and phenomena. Time-dependent multiple reactions and processes, distributed laterally across surfaces as well as throughout interfacial films, lead to system behavior that is difficult to analyze. The influence of geometry, thermodynamics, kinetics, transport processes, and the nature of the surface and environment may all be important. In addition, the mechanical state of a degrading interface may affect phenomena such as stress corrosion cracking or film cracking and delamination. One justification for modeling and analysis is that judicious modeling, combined with experiment, is generally less expensive than experimentation alone. Mathematical models (once established) have quantitative predictive capabilities for accelerated testing, and for scale-up and scale-down. The models have the additional benefit that they provide general insight that may translate into understanding other corrosion phenomena as well.

Accelerated life testing cannot be meaningfully interpreted without reliable understanding of the degradation mechanisms occurring in the corrosion processes (see Chapter 25 of this volume). This need requires more extensive and basic modeling efforts than have been characteristic of corrosion studies in the past. To be useful to an accelerated testing program, modeling must take place both at the microscopic and macroscopic time and length scales, and it must take place in close coordination with carefully controlled experimental programs to verify the concepts and parameters in the models. Relevant modeling technologies include, at the electronic level, band structure methods and their extensions to disordered systems; at the atomic level, molecular dynamics methods and electronic structure methods; and at the macroscopic level, Monte-Carlo and engineering methods of simulation. Taken together, the goal of the modeling efforts discussed in the report is to provide predictions and simulations of systems (e.g., automobiles, buses, and trucks) so that they are relatively trouble-free for extended periods of service.

V. RECOMMENDATIONS

A. Systems Near Success

Surface modification has advanced the state of the art in corrosion protection in several of the transportation and solar energy technologies. Improvements in protection systems would provide the incremental advances needed to achieve desired lifetimes. The economic savings would be large.

First, enormous resources are currently devoted to corrosion prevention by Zn galvanizing of steel parts in U.S. vehicles. Opportunities to reduce these costs arise from the existence of new galvanizing alloys and from the possibility of greatly improved understanding of the structures and processes associated with galvanic protection afforded by these alloys using modern surface science characterization and modification techniques.

- Recommendation: We recommend significant new programs to characterize and improve galvanizing alloys on steel.

Second, primary parabolic mirrors fabricated for solar energy collectors consist of PMMA/Ag/adhesive/Al or stainless steel multilayer assemblies. Corrosion of the Ag occurs beneath the PMMA.

- Recommendation: Research to understand the interface degradation reactions and mitigate the cause of the reaction and/or to develop a UV degradation-resistant, inexpensive coating to replace PMMA should be conducted.

Third, single-crystal Si solar cells can compete with amorphous and polycrystalline Si solar cells for terrestrial applications when less expensive materials and fabrication procedures are substituted in production. In these, solar cells are encapsulated under a glass cover (substituted for fused quartz) using ethylene vinyl acetate for environmental protection. The pottant is subject to UV photothermal degradation and may chemically react with Ag or Al metallization (substituted for Pd/Ag) on the solar cell surface, thereby degrading performance because of optical losses, reactions with degradation products, and unbalancing the cell circuitry.

- Recommendation: Research should be conducted to develop a UV stable, organic, or inorganic pottant to encapsulate the solar cell and bond to the cover glass.

B. Surface Characterization

Surface characterization of corroded surfaces and of protective coatings and films is on the threshold of significant advances, particularly as a consequence of the recent development of improved in situ techniques.

- Recommendation: Programs are recommended that will exploit and further develop new in situ surface characterization methods for applications to corrosion problems (see Chapter 26 in this volume).

C. Surface Modification and Surface Characterization of Emerging Systems

First, the increasing use of light metal alloys—notably aluminum and magnesium—in vehicles will increase fuel efficiency dramatically. Corrosion and wear limit alloy life, and surface modification becomes an essential part of the application.

- Recommendation: We recommend programs to design these surfaces for light-metal alloys and alloy composites, guided by modern surface/interface characterization techniques.

Second, commercialized, electrochromic windows will provide a dramatic energy savings in the nation's buildings. Electrochromic systems have not yet demonstrated the long-term durability required in this application. Because this is an emerging technology, fundamental understanding of the materials, interfaces, and degradation mechanisms should be carried out to underpin its widespread use.

- Recommendation: We recommend characterizing technologically feasible electrochromic systems using surface and interface characterization techniques and then solving any life-limiting problems with advanced surface modification.

Third, electric vehicles will require better power sources than the lead-acid battery currently available. These advanced batteries and fuel cells must withstand extended cycling under a broad range of driving conditions. Typically corrosion limits the life of an electrochemical power source.

- Recommendation: We recommend specific efforts be devoted to identifying corrosion phenomena in batteries and fuel cells for electric vehicles and then finding the solutions with surface modification.

D. Basic Research in Corrosion

The way to future progress in corrosion protection must be paved by ongoing basic research. Knowledge of the mechanisms of corrosion, its prevention, inhibition, and repair are the stepping stones for advances in new materials and processing.

- Recommendation: We recommend that the basic studies of surface modification and characterization be expanded by long-term commitments, to reveal the processes by which coatings and films fail, and to advance general methods of corrosion protection.

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21. BATTERIES AND FUEL CELLS

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ABSTRACT

Electrochemical energy systems are dominated by interfacial phenomena. Catalysis, corrosion, electrical and ionic contact, and wetting behavior are critical to the performance of fuel cells and batteries. Accordingly, development of processing techniques to control these surface properties is important to successful commercialization of advanced batteries and fuel cells. Many of the surface processing issues are specific to a particular electrochemical system. Therefore, the working group focused on systems that are of specific interest to the DOE Office of Conservation and Renewable Energy. The systems addressed were:

- Polymer electrolyte membrane (PEM) fuel cells
- Direct methanol oxidation (DMO) fuel cells
- Lithium/polymer batteries.

The approach used by the working group for each of these systems was to follow the path of the current through the system and to identify the principal interfaces. The function of each interface was specified together with its desired properties. The degree to which surface properties limit performance in present systems was rated. Finally, the surface processing needs associated with the performance-limiting interfaces were identified. This report summarizes this information.

I. INTRODUCTION

For identifying and prioritizing the research needs and opportunities in its topical area, the working group on Batteries and Fuel Cells focused on electrochemical energy systems that are of specific interest to the DOE Office of Conservation and Renewable Energy. The systems addressed were:

- PEM fuel cells
- DMO fuel cells
- Lithium/polymer batteries.

The approach used by the working group in each of these systems was to follow the path of the current through the system and to identify the principal interfaces. The function of each interface was specified together with its desired properties. The degree to which surface properties limit performance in present systems was rated. Finally, the surface processing needs associated with the performance-limiting interfaces were identified.

II. PEM FUEL CELLS

A. Introduction to PEM Fuel Cells

Fuel cells offer a means of electricity production with a higher efficiency and a lower pollutant emission than other technologies. Basically, a fuel cell converts the chemical energy in hydrogen and oxygen to electricity with water as the by-product. The oxygen can be supplied directly as air, and the hydrogen is available from a broad range of energy resources. These resources include reformed organic fuels such as methanol or natural gas, reformed biomass, solar-electric-driven electrolysis, wind-powered electrolysis, and other renewable resources.

Phosphoric acid, molten carbonate, and solid oxide fuel cells are being developed for stationary power plant applications. However, for transportation and a broad range of other applications such as private homes and small businesses, remote site generation, and some industrial uses, compact, efficient, low-cost fuel cells are needed.

The PEM fuel cell has a combination of characteristics that are particularly attractive for these applications. It provides high power densities. It can tolerate CO_2 in the fuel stream, allowing the use of reformed organic fuel. It can be self-starting at temperatures above ~ 20°C. Low-cost structural materials can be used because of the low operating temperature and reduced corrosion, and the solid character of the electrolyte facilitates sealing and safety of the fuel cell stack. The limitations of the technology have been high platinum content, expensive membranes, poor carbon monoxide tolerance, water management problems, and difficulty in thermally integrating the fuel cell with a reformer. Several of these problems can be solved by modifying or improving the surface properties of the materials and components of the fuel cell.

B. Surface Processing Aspects of PEM Fuel Cells

Figure 1 shows a generalized cross-section of a polymer electrolyte fuel cell. To emphasize the surface processing aspects, each of the elements of the fuel cell is shown separately. In real fuel cell designs, two or more of these elements may be combined in a multifunction element.

In considering the surface processing aspects of the fuel cell, two classes of surfaces must be considered. The first class includes the interfaces between the elements, such as the interface between the anode and the membrane. The second class involves surfaces within an element, such as the pore surfaces within the gas diffusion structure.

The working group evaluated each of the elements shown in Fig. 1, moving from left to right. The function each element must provide was specified, and the properties that would be desired to achieve that function were identified. Each of these properties was then evaluated to determine whether the property is dominated by the surface. Finally, the importance of improving the surface properties was rated as high, medium, or low. This information is summarized in the tables below. For those interfaces that currently limit the performance of the fuel cell, suggestions for specific research and development efforts are indicated.

Table 1. End Plate/Gas Separator Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Mechanical compression	Uniform pressure	No	Low
	Corrosion resistant	Yes	Low
Electrical contact	Low contact resistance	Yes	Low
	Long-term stability	Yes	Low

The interface between the end plate and the gas separator does not present a significant limitation on performance.

Table 2. Gas Separator/Gas Distribution Interface

Function	Desired Properties	Surface Dominated	Problem Severity
H_2/O_2 isolation	Gas impermeability	Possible	Low
	Corrosion resistant	Yes	Medium
Electrical contact	Low contact resistance	Yes	Low
	Long-term stability	Yes	Low

Note: In many designs, the function of the gas separator and the gas distribution plate are combined in a grooved impermeable plate.

Performance and design flexibility of this interface would be increased by

- Developing corrosion-resistant, electrically conductive coatings or
- Developing surface modification for enhanced corrosion resistance.

Table 3. Gas Distribution/Anode Gas Diffusion Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Gas distribution across electrode	Low pressure drop	No	Low
	Good fuel utilization	No	Low
Electrical contact	Low contact resistance	Yes	Low
	Corrosion resistant	Yes	Medium

Performance and design flexibility of this interface would be increased by

- Developing corrosion-resistant, electrically conductive coatings or
- Developing surface modification for enhanced corrosion resistance.

Table 4. Gas Diffusion/Anode Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Gas distribution across electrode	Low gas diffusion resistance	Possible	Medium
	Minimize CO_2 diffusion barrier	Possible	Medium
Electrical contact to anode	Good electrical contact to catalyst	Yes	Medium
	Corrosion resistant	Yes	Medium

Performance and design flexibility of this interface would be increased by

- Improving the characterization of the interface
- Modeling the gas composition within the pores as a function of operating conditions
- Using surface treatment to improve the electrical contact.

Table 5. Anode Electrochemical Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Rapid hydrogen oxidation	High gas permeability	Possible	Medium
	Good electronic contact	Yes	Medium
	Good ionic contact	Yes	Medium
	High catalytic activity	Yes	Medium
	CO tolerant	Yes	High
	Resistant to other poisons	Yes	High
	Corrosion resistant	Yes	Medium

Note: In a fuel cell, the hydrogen is catalytically oxidized at the anode. This reaction requires the catalytic site to be in contact with hydrogen gas, an electrical conductor, and a hydrogen ion conductor. In the PEM fuel cell, the hydrogen ion conductor is a hydrated ionomer. The water content of this ionomer must be maintained over the full operating range of the fuel cell. Moreover, the catalytic reaction is strongly affected by the water concentration at the catalytic site. Poisoning from CO or other contaminants in reformed organic fuels is also a severe problem.

Performance and design flexibility of this interface would be increased by

- Improving water transport to the catalytic sites
- Developing catalysts with improved impurity tolerance
- Modeling the ionic and electronic properties of micro-porous composites
- Improving the understanding of hydrogen oxidation kinetics at ionomer/catalyst interfaces.

Table 6. Anode/Ionomer Membrane Interface

Function	Desired Properties	Surface Dominated	Problem Severity
H^+ ion conduction from anode	Good ionic contact	Yes	Medium
	Maintain water balance at anode	Possible	High
	Long-term stability	Yes	Low
Prevent gas diffusion between anode and cathode	Gas impermeability	Possible	Medium

Performance and design flexibility of this interface would be increased by

- Determining the role of membrane surface properties
- Improving the control of the surface functionality by chemical surface modification
- Developing an ionically conductive adhesive that could be used to bond the anode to the membrane.

Table 7. Ionomer Membrane/Cathode Interface

Function	Desired Properties	Surface Dominated	Problem Severity
H^+ ion conduction to the cathode	Low ionic contact resistance	Yes	Medium
	Maintain water balance	Possible	High
	Prevent gas diffusion between anode and cathode	Possible	Medium
	Long-term stability	Possible	Medium

Performance and design flexibility of this interface would be increased by

- Determining the role of membrane surface properties
- Improving the control of the surface functionality by chemical surface modification
- Developing an ionically conductive adhesive that could be used to bond the cathode to the membrane.

Table 8. Cathode Electrochemical Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Rapid oxygen reduction	High oxygen permeability	Possible	Medium
	Good electronic contact	Yes	Medium
	Good ionic contact	Yes	Medium
	High catalytic activity	Yes	High
	Rapid product water removal	Possible	High
	Resistant to poisons	Yes	High
	Corrosion resistant	Yes	Medium

Note: In a fuel cell, oxygen is catalytically reduced at the cathode. This reaction requires the catalytic site to be in contact with oxygen gas, an electrical conductor, and a hydrogen ion conductor. In the PEM fuel cell, this reaction is usually the kinetically limiting reaction. Platinum or platinum alloys are the only catalysts found so far that show high reaction rates in this environment. This catalytic reaction is also strongly affected by the water concentration at the catalytic site. Removal of product water from the catalytic site is critical to sustaining high performance.

Performance and design flexibility of this interface would be increased by

- Developing alternatives to platinum as an oxygen reduction catalyst
- Improving the understanding of hydrogen oxidation kinetics at ionomer/catalyst interfaces.

A DOE-sponsored workshop on oxygen electrocatalysis was held October 29-November 1, 1991. Detailed recommendations for research and development on the fuel cell cathode can be found in the proceedings of that workshop [1].

Table 9. Cathode/Cathode Gas Diffusion Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Gas distribution to catalyst	Rapid oxygen diffusion	Possible	Medium
Electrical contact to catalyst	Good electrical contact to catalyst	Yes	Medium
	Corrosion resistant	Yes	Medium

Performance and design flexibility of this interface would be increased by

- Determining the effects of potential cycling on corrosion of this interface
- Determining the microscopic effects of pressure
- Developing improved contact by surface treatment.

Table 10. Cathode Gas Diffusion Layer—Internal Surfaces

Function	Desired Properties	Surface Dominated	Problem Severity
Gas distribution across electrode	Low gas diffusion resistance	Possible	Medium
	N_2 removal	Possible	Medium
Product water removal	Hydrophobic	Yes	Medium
	Good water droplet transport	Yes	High
	Long-term stability	Yes	High

Performance and design flexibility of this component would be increased by

- Improved surface treatment to maintain hydrophobicity over long periods
- Tailoring of the porosity to facilitate gas exchange
- Modeling of the two-phase transport in porous structures.

The remaining interfaces in the PEM fuel cell on the cathode side are similar to those on the anode side with similar surface processing issues.

C. PEM Fuel Cell Summary

The areas of improvement most needed in the PEM fuel cell are lower cost, water management, and impurity tolerance. Surface processing can make a contribution in each of these areas. Development of conductive, corrosion-resistant coatings can reduce the cost of the structural materials. Development of processes to provide pore surfaces with hydrophobic properties that are stable over thousands of hours of operation can improve the performance and lifetime of the fuel cell. Development of catalysts with a better impurity tolerance and a lower cost than platinum can improve the fuel flexibility and reduce the cost of PEM fuel cells.

III. DMO FUEL CELL

A. Introduction to DMO Fuel Cells

In a DMO fuel cell, methanol is supplied directly to an anode catalyst without the need for reforming. Although high-temperature systems such as solid oxide fuel cells operating at ~ 1000°C and molten carbonate fuel cells operating at ~ 600°C have the potential to use methanol directly as a fuel, DMO fuel cells usually refer to relatively low-temperature systems operating at 25°C to 300°C, in which the methanol is catalytically oxidized in the presence of water to produce hydrogen ions, electrons, and carbon dioxide.

The benefits of a DMO/air fuel cell become apparent when it is compared with today's fuel processing technology. A number of approaches have been used to convert organic fuel, and in particular methanol, to a hydrogen-rich fuel gas. These include high-temperature reforming, low-temperature reforming with selective oxidation, and low-temperature internal reforming coupled with selective oxidation within the anode chamber. All of these approaches have significant drawbacks, particularly in system cost and complexity.

DMO fuel cells, in principal, eliminate the need for fuel reforming and thus offer the potential for a lower cost and a smaller power plant size. They also offer safety advantages by eliminating the need to handle hydrogen. Finally, DMO fuel cells may have a better transient response than reformer-based power systems. The problems with DMO fuel cells are, however, also very difficult.

B. Surface Processing Aspects of DMO Fuel Cells

In many respects, the surface processing issues associated with DMO fuel cells are similar to those associated with PEM fuel cells. However, there are a set of special problems that are characteristic of DMO fuel cells that will be addressed in this section. These problems are (1) rapid poisoning of the anode catalyst by products of the methanol oxidation, such as CO and (2) methanol cross-over from the anode to the cathode, which poisons the cathode catalyst.

There are two primary approaches to solving problem (1). The first is to find a catalyst that desorbs reaction products such as CO. The most promising catalysts of this type are PtRu alloys, which may have additional components. Further research to identify a superior DMO catalyst is important to the development of this technology.

The second approach to solving problem (1) is to increase the operating temperature to the point at which products such as CO can be thermally desorbed from the catalyst. A temperature of 200°C to 300°C would be desirable for this purpose. However, existing membrane separators are not stable at such elevated temperatures. The development of a stable membrane with high ionic conductivity would be very important to the further development of DMO fuel cells. This is primarily a materials development issue rather than a surface processing issue, but there may be surface processing aspects to the fabrication of such a membrane.

Conventional membrane separators such as Nafion® are permeated by methanol, and methanol that reaches the cathode rapidly poisons the oxygen reduction reaction. One solution to this problem is to develop a membrane that is impermeable to methanol but retains the other desired properties for a fuel cell. Again, this is primarily a materials development issue; however, it may be possible to modify the surface of useful membranes to block methanol feed-through without destroying the other desirable features. This is an important line of research.

C. DMO Fuel Cell Summary

The issues associated with the DMO fuel cell have been dealt with in great detail in a Direct Methanol Oxidation Workshop held at Georgetown University on May 14-16, 1990. The recommendations from that meeting are contained in the workshop summary [2].

IV. LITHIUM-POLYMER BATTERIES

A. Introduction to Lithium-Polymer Batteries

Fenton and Wright observed in 1973 the remarkable conductivity of lithium salts in polyethylene oxide [3]. Armand drew attention to the practical application of these polymer electrolytes in lithium batteries [4]. Shortly after this work, two groups—one headed by the Harwell Research Laboratories and the other headed by Hydro Quebec—were established to attempt commercialization of the technology.

In the intervening years, increased understanding of the ion conduction mechanism in the polymers has occurred. It has been realized that conduction primarily occurs in amorphous phases of the electrolytes. Simple polyethylene oxide electrolytes are sufficiently amorphous above 80°C to have conductivities above $10^{-4}\,W^{-1}cm^{-1}$. For thin films, conductivities above $10^{-4}\,W^{-1}cm^{-1}$ are sufficient to meet the power requirements of electric vehicle batteries. It is desirable to have this performance from a battery at ambient temperatures.

Recent work on the polymer electrolytes has resulted in the development of electrolytes that are amorphous at ambient temperatures and have conductivities in the range of $10^{-3}\,W^{-1}cm^{-1}$. With this development, there is now a strong initiative to commercialize the lithium polymer battery.

Another key development, important to the lithium polymer battery, was lithium intercalating cathode materials, first proposed by Wittingham [5]. With this development, "the physicist's battery" was possible. In this system, the lithium moves back and forth between the cathode and anode without undergoing significant chemical reactions to new chemical entities. The electrolyte does not participate in the charge/discharge reactions, so it can be very thin, as long as it provides separation between the electrodes.

With these developments, the thin-film solid-state lithium battery is a reality. Typically the construction is

(1) Pure lithium metal in the range of 25-mm to 50-mm thick, a graphite carbon/lithium intercalation material, or a lithium-aluminium alloy

(2) A polymer electrolyte in the range of 50-mm to 150-mm thick

(3) A cathode mixture prepared from a lithium intercalating transition metal oxide powder laminated into a film approximately 100-mm thick.

The addition of current collectors and a sealed envelope completes the battery.

B. Surface Processing Aspects of Lithium-Polymer Batteries

Figure 2 shows a generalized cross-section of a lithium-polymer battery. To emphasize the surface processing aspects, each of the elements of the battery is shown separately.

In considering the surface processing aspects of the battery, two classes of surfaces must be considered. The first class includes the interfaces between the layers, such as the interface between the lithium-anode and the polymer electrolyte. The second class involves interfaces within a layer, such as the interfaces between transition-metal-oxide particles and the polymer electrolyte.

The working group evaluated each of the elements shown in Fig. 2, moving from left to right. The function each element must provide was specified, and the properties that would be desired to achieve that function were identified. Each of these properties was then evaluated to determine whether the property is dominated by the surface. Finally, the importance of improving the surface properties was rated as high, medium, or low. This information is summarized in the tables below. For those interfaces that currently limit the performance of the lithium battery, suggestions for specific research and development efforts are indicated.

Table 11. Current Collector/Lithium Anode

Function	Desired Properties	Surface Dominated	Problem Severity
Electrical contact	Low contact resistance	Yes	Low
	Long-term stability	Yes	High

The interface between the current collector and the lithium anode is subject to corrosion. Surface treatments to reduce this corrosion or processing to reduce the activity of the lithium metal would help solve this problem.

Table 12. Lithium Anode/Polymer Electrolyte Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Li^+ ion conduction	Good ionic contact	Yes	Medium
	Reversible Li deposition and stripping	Yes	High
	Long-term stability	Yes	High

The long-term performance of the lithium/polymer battery can deteriorate due to passivation at the Li/polymer electrolyte interface. This passivation process is not yet understood. Research is needed to identify the passivation mechanism and to develop materials techniques that will retard the passivation process.

Table 13. Polymer Electrolyte/Intercalation Electrode Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Li^+ ion conduction	Good ionic contact	Yes	Medium
	Reversible Li^+ insertion and withdrawal	Possible	Medium
	Long-term stability	Yes	High

Interfaces between the polymer electrolyte and intercalation compounds such as vanadium oxide are also affected by passivation problems. The resistance of this interface can increase by large factors over a period of a few hundred hours [6]. Research is needed to identify the passivation mechanism and to develop materials techniques that will retard the passivation process.

Another stability problem is manifested by capacity decline during cycling. This may be due to electrical isolation of some of the electrode particles in the composite caused from repeated intercalation-deintercalation cycles. The changes in particle volume during these cycles may deteriorate the interparticle contact. This problem is surface related and requires careful characterization to determine the cause. Surface processing may also provide a potential solution to this problem.

Table 14. Intercalation Electrode/Current Collector Interface

Function	Desired Properties	Surface Dominated	Problem Severity
Electrical contact	Low contact resistance	Yes	Low
	Long term stability	Yes	Low

The interface between the intercalation electrode and the current collector does not present significant surface processing problems.

C. Lithium-Polymer Battery Summary

The key problem associated with lithium-polymer batteries is long term stability. The loss in performance can be due to passivation of internal interfaces or to corrosion. Surface analysis is an important tool to diagnose the cause of these problems, and surface processing techniques need to be developed to minimize these effects.

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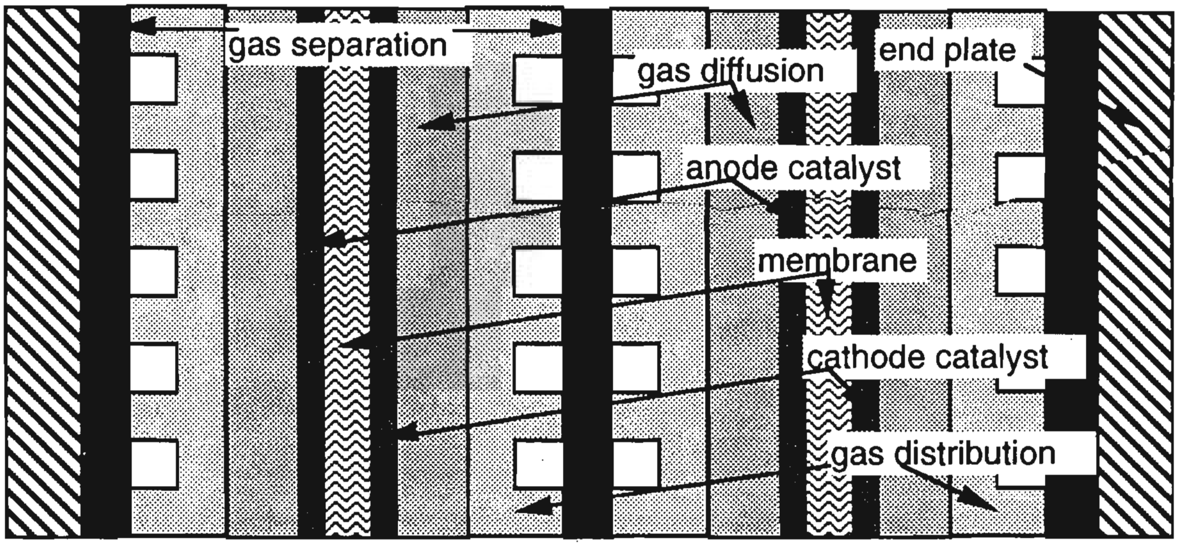

Figure 1. Schematic cross-section of a polymer electrolyte fuel cell

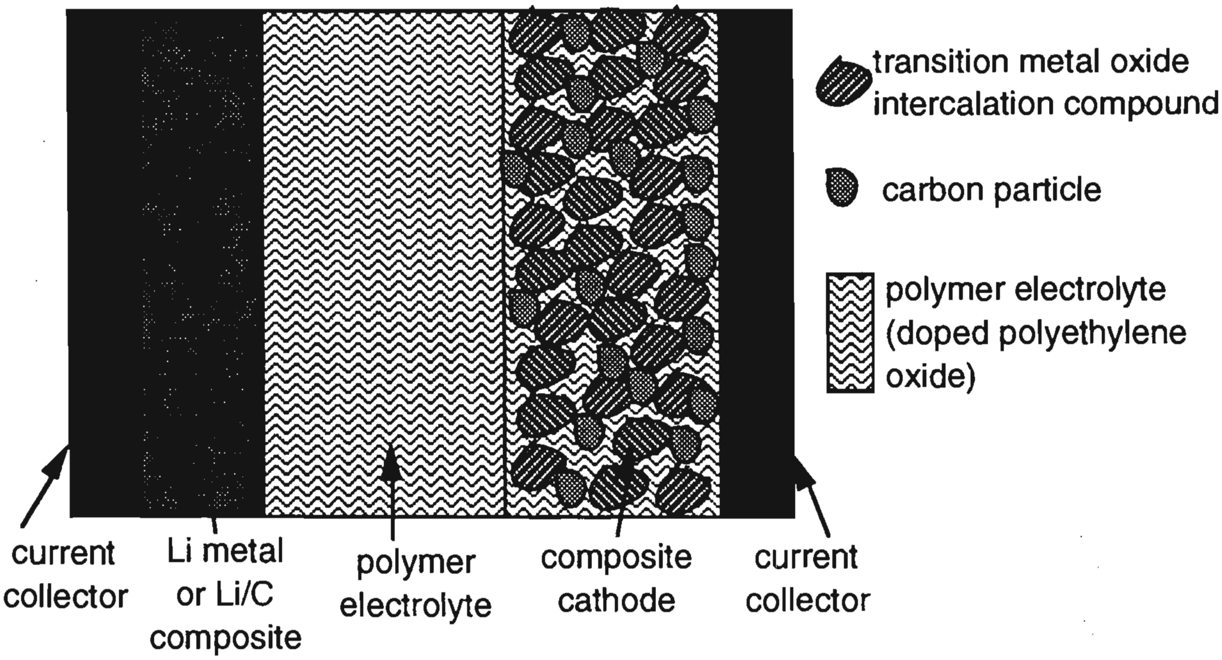

Figure 2. Schematic cross-section of a lithium polymer electrolyte battery

22. LUBRICATING AND WEAR SURFACES

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I. IDENTIFIED NEEDS AND OPPORTUNITIES

The working group identified 19 problems related to lubricating and wear surfaces as they apply to transportation technologies. Because the problems are quite diverse in nature, they are treated as 19 separate issues using the format, in general, of problem, current approach, needs, R&D program envisioned, time scale, and payoff.

A. High-Temperature Valve Guide/Stem Wear

Problem: Valve guide/stem wear at high temperatures in developmental low-heat-rejection engine.

Current approach: 4140 steel valves/cast iron guides at 300°-350°C.

Needs: Coating on either or both surfaces to extend operating temperature to 500°C and to reduce liquid lubricant requirement.

R&D program envisioned: Investigation of coating/material combinations with high-temperature, 20,000-h capability; should provide lubricious interface.

Time scale: 5-7 years.

Payoff: Maintain international competitive advantage, better fuel efficiency, and reduced emissions.

B. Piston Ring/Bore Tribosystem

Problem: Piston ring/bore tribosystem needs improvement to decrease wear, oil consumption, and emissions for gasoline, diesel, and alternative fuels.

Current approach: Coated piston skirts and rings/cast-iron or Al bores at ≈ 150°C for 500,000 miles (diesel), 100,000 miles (automobile).

Needs: Heavy-duty diesel—serviceable ring/bore combination at ≈ 300°C for approximately 1,000,000 miles, 20% increase in cylinder pressure, and reduced friction.

Automotive: Friction reduction at current temperatures for 200,000 miles.

R&D program envisioned: Identify/develop materials (coatings)/processes for high-temperature tribological interfaces, e.g., plasma-spray, chemical vapor deposition (CVD)/physical vapor deposition (PVD). Develop improved piston ring/cylinder wall tribological computer models to guide research.

Time scale: 5-7 years.

Payoff: Maintain international competitive advantage, better fuel efficiency, and reduced emissions.

C. Load-Carrying Capacity: Gears and Bearings

Problem: Need increased load-carrying capacity for gears and bearings in spark-ignited/diesel engines and vehicular drive trains, as well as in manufacturing.

Current approach: Steel (various) with some type of wear-life-enhancement process.

Needs: Improvements in power throughput capability to allow components with lower cost or smaller size to be used.

R&D program envisioned: Improved computer modeling of gears and bearings. Investigate coatings or new surface treatments that offer reduced pitting, scoring, or galling in comparison with conventional materials.

Time scale: 8-10 years.

Payoff: Enhanced international competitiveness, improved reliability, and design flexibility.

D. Engine Durability with Methanol

Problem: Engine durability with methanol fuels is a current concern. In particular, upper cylinder bore wear has been observed near the top dead center (TDC) position in some tests. Low-temperature operation is the most severe mode of operation. Causes cited include formation of formic acid from methanol combustion, displacement of oil/oil additives from the surface by methanol, and poor lubrication due to emulsion formation.

Current approach: Engines currently designed for rapid heat-up and selection of methanol-compatible oils. Methanol-compatible oils have higher acid-neutralizing ability and other proprietary features.

Needs: Surface treatments for piston rings and/or bores to provide methanol-compatible coatings for cast iron and potentially for other substrates.

Payoff: Assured long-term durability for flexible-fueled vehicles, conformance with corporate average fleet economy (CAFE) requirements, and international competitive advantage.

E. Continuously Variable Transmissions

Problem: Belt and sheave continuously variable transmissions (CVTs), coupled with small-displacement engines, are currently in operation. Scale-up of this technology has been limited in part by wear of sheaves and belts. Predominant wear mechanisms include fatigue and plastic deformation under high pressures and low sliding speeds.

Current approach: Selection of more fatigue-resistant alloys. Improved surface hardening.

Needs: Fatigue- and plastic-deformation-resistant material, surface treatment, or coating. Improved model development for optimizing design and minimizing wear.

Payoff: Fuel-economy benefits and improved international competitive advantage.

F. Immersed Electric Fuel Pumps

Problem: Electric fuel pumps operate immersed in fuel. Potential wear areas include the commutator/brush interface. Concerns include potential abrasion and arcing. The effect of methanol fuel on these phenomena has not been established. Other rubbing contacts are potential concerns because of the poor lubricating ability of these (low-viscosity) fuels.

Current approach: Issues are in the early stages of investigation.

Needs: Identification of materials/coatings appropriate for commutator, brush, and other applications with gasoline, methanol, and admixtures.

Payoff: Improved reliability and design flexibility.

G. Tribological Materials Selection from Accelerated Tests

Problem: Accelerated or bench tests used for selection of tribological materials do not always accurately model the effects of actual service. This deficiency may lead to unrealistic failure modes during testing, or conversely to unexpected failures during service. No widely accepted, quantitative adhesion evaluation method is presently available for bond strengths in excess of 69 MPa (10 ksi).

Current approach: Varies widely from case to case, ranging from well-defined and verified accelerated wear tests to arbitrary screening tests for wear and/or adhesion.

Needs: Systematic procedures for defining appropriate tests.

Payoff: Rapid material screening and validation, reduced costs and improved performance, shorter cycle time.

H. Tribology Data Base

Problem: The need exists for an expanded, user-friendly, readily available tribology data base. Definition of surface composition required for proposed new applications tends to be "ad hoc" and dependent on prior experience. This may lead to use of less-than-optimal material or even to component failure during service.

Current approach: Prior experience and consultation with in-house experts and vendors.

Needs: User-friendly access to information generated by previous research. Perhaps the presently available ACTIS (a computerized tribology information system) family software package could be expanded to include a data base on surface processing. Expert systems for surface processing selection should be explored.

Payoff: Improved product performance, reduced cost, shorter cycle time.

I. Improved Transmission Performance and Durability

Problem: Optimum shift performance and durability of vehicular transmissions depend on matching friction materials, fluid properties, and design/operational parameters. No systematic body of knowledge interrelating these factors is available to U.S. original-equipment manufacturers (OEMs).

Current approach: United States—reliance on vendors and experts, empirical testing. Japan—OEM-vendor-university research has been ongoing.

Needs: United States—OEM-vendor-university research, perhaps including government laboratories to define friction material, fluid, and design parameters.

Payoff: Improved vehicle shift performance and durability, international competitive position for U.S. OEMs and vendors.

J. Adhesive Wear of Injection Plunger Barrel

Problem: Injector plunger-barrel scuffing (adhesive wear) with diesel fuel, but especially with alternative (low-lubricity) fuels. Potentially also a problem with spark-ignition engines utilizing alternative fuels.

Current approach: Typically, electroplated hard-chromium plunger with hardened steel bore, or nitrided plunger and bore. Very tight clearances required, e.g., 2.5 μm (100 μin.) diametral. Fuel-lubricated, approximately 93°C (200 °F). Axial load to 12 kN (2600 lbf), injection pressure ≈ 172 MPa (25 ksi). Required life > 500,000 miles.

Needs: Injection pressure ≈ 207 MPa (30 ksi), up to 1,000,000 miles for heavy-duty engines. Greater tolerance to low-lubricity fuels (e.g., low S, low aromatics fuel, arctic fuel, methanol, etc.)

R&D program envisioned:

- Develop scuffing- and wear-resistant coatings.
- Develop solid lubricating coatings.
- Evaluate diamond-like-carbon coatings—need improved adhesion to steel.
- Develop coating process for long, narrow bores (l/d > 3), e.g., conformal-plasma ion implantation.
- Bench/screening tests and engine tests required.

Time scale: 3-year R&D program to develop and evaluate processes.

Payoff:

- Improved emissions/fuel economy (higher injection pressure)
- Improved durability and reliability with low-lubricity fuels

- Improved international competitiveness.

K. Enlargement of Injector Spray Holes (Diesels)

Problem: Gradual enlargement of injector spray holes of diesel fuel injectors by erosion-corrosion mechanism, leading to increased fuel consumption, higher emissions.

Current approach: Carburized steel injector cup with multiple holes formed by electrodischarge machining (EDM). Hole diameter approximately 200 μm (0.008 in). Injection pressure ≈ 172 MPa (25 ksi). Diesel fuel contaminated with sulfuric acid/organic acids/combustion products, 150°-315°C (300°-600°F). Required life > 10,000 h or 700,000,000 cycles.

Needs: Reduce erosion-corrosion rate by factor of 5.

R&D program envisioned:

- Develop thin PVD coating processes for long, narrow holes (l/d > 4); evaluation.
- Develop ion-implantation process for long, narrow holes. Evaluate materials.
- Determine effectiveness of current line-of-sight processes for reducing erosion/corrosion rates.

Time scale: 5-year R&D program.

Payoff:

- Improved durability (fuel economy/emissions)
- Increased fuel-injector pressure capacity (lower emissions/fuel economy)
- Improved international competitiveness.

L. Diesel Fuel Injector Plunger Tip-Cup Seating

Problem: Need to reduce diesel fuel injector plunger tip-cup "beat in," to allow use of higher injection pressures. Needle and seat of natural-gas injectors also need to survive "beat in" with low-lubricity fuels.

Current approach: Typically tool-steel plunger, carburized steel cup, axial load to 12 kN (2600 lbf), approximately 172 MPa (25 ksi) injection pressure. Diesel fuel contaminated with water/organic acids/combustion gases at 150°C (300°F). Impact velocity of approximately 2.2 m/s (85 in/s). Required life > 10,000 h (700,000,000 cycles). Needle and seat of natural-gas injectors use nitrided steel.

Needs: Increase in injector travel within functional specifications at 207 MPa (30 ksi) injection pressure. Durable coatings for natural-gas injectors.

R&D program envisioned: Develop hard, thin-film coatings with sufficient ductility and adhesion to the substrate for this application, yet with low adhesion to counterface. Ion beam assisted deposition (IBAD) and ion-surface modification (ISM) are possible techniques.

Time scale: 3 years.

Payoff: Increased fuel-injection pressure capability (improved emissions/fuel economy). Improved international competitiveness.

M. Lifetime of Cams and Cam-Roller Followers

Problem: Improved rolling-contact-fatigue (RCF) life of cams and cam-roller followers is needed.

Current approach: Induction-hardened steel, powder-metallurgy and cast-iron cams, steel or ceramic rollers. Required life > 500,000 miles (heavy duty) and 100,000 miles (automotive); oil-lubricated. Hertz stress approximately 1.4-2.0 GPa (200-300 ksi).

Needs: Increase injection pressure 20% without reducing RCF life. Improved lifetime for ceramic rollers.

R&D program envisioned:

- Evaluate thin-film ceramic PVD coatings on cam lobes.
- Evaluate thin-film solid lubricating coatings on roller pin to reduce roller-pin friction, hence cam-roller traction.

Time scale: 3 years.

Payoff: Increased fuel-injection pressure capability (improved emissions/fuel economy). Improved international competitiveness.

N. Load-Carrying Capacity and Corrosion Resistance of Bearings and Bushings

Problem: Future designs will result in increased loads on journal bearings (higher cylinder pressure, higher injection pressure) and increased oil temperatures; hence need to improve load-carrying capacity and reduce corrosion of bearings and bushings.

Current approach: Typically high, lead-tin bronze bushings cast or sintered onto steel backs, with Pb-Sn overlay. Oil-lubricated.

Needs: Increase load-carrying capacity by 20%. Increase oil temperature from ≈ 120°C to ≈ 150°C (250°-300°F).

R&D program envisioned: Evaluate advanced thin-film solid lubricating coatings as alternatives to current overlay materials.

Time scale: 3-5 years.

Payoff: Improved fuel economy/emissions due to higher cylinder pressure, injection pressure. Reduced friction from (possibly) higher sump temperatures. Decreased Pb in environment. Improved international competitiveness.

O. Self-Lubricating and Scuffing-Resistant Materials

Problem: Surfacing of lightweight materials for self-lubrication and resistance to scuffing. Examples include aluminum block engine—cylinder bore surface, valvetrain components (valves, tappets, etc.), transmission case "hot spots," and lightweight brake rotors, and air conditioning (A/C) compressor hardware.

Current approach: Use of inserts—e.g., bore liners (cast iron), valve seats, etc., and use of heavier, wear-resistant (usually ferrous) alloys.

Needs: Understanding adhesion of surfacing layers to metals such as aluminum; modeling for mechanical surface behavior of bimaterials couples; understanding of methodologies for selecting composite surfaces.

Time scale: 3-5 years.

Payoff: Reduced friction and energy consumption; manufacturing simplification (in some cases).

P. Correlation Between Surface Modification and Performance of Materials in Lubrication Systems

Problem: Lack of understanding of surface-preparation processes of multiphase materials and performance in lubricated systems. Examples include A/C compressors, engine cylinder bores, valvetrain componentry.

Current approach: Trial and error, past knowledge, existing tribomodels for lubricated contacts.

R&D program envisioned: Understanding of the topographic and compositional influence of multiphase material systems and machining/finishing processes relative to the limits of performance with regard to boundary lubrication, friction, and such features as noise and vibration. Extensive use of tools such as atomic-force microscopy (AFM), surface spectroscopies, etc., is envisioned.

Time scale: 5+ years.

Payoff: Highly finished, more "forgiving" mechanisms in terms of reliability, durability, and customer-satisfaction issues such as noise and vibration. Improved product performance, reduced cost, shorter cycle time.

Q. Lifetime of Nonferrous Die Materials

Problem: The wear life of nonferrous die materials is insufficient for medium-volume applications.

Current approach: Hard-chromium plating is being evaluated; nothing else.

Needs: A wear-life-enhancement process that can be easily applied, can give increased tool life, and can be repaired, stripped, and retreated if needed.

R&D program envisioned: Hard-chromium plating and plasma-source ion implantation appear to be potential solutions.

Time scale: Process could be used immediately. R&D program could require 2-3 years.

Payoff: Benefits to U.S. auto-makers and other U.S. manufacturers include obtaining cheaper tooling, faster time to market, reduced lead time, and products competitive with foreign companies.

R. Lifetime of H-13 Tool Steel Foundry Patterns Used with Molten Aluminum

Problem: Molten aluminum attacks foundry patterns and core pins made out of H-13 tool steel; this results in many premature failures.

Current approach: Patterns sprayed with a graphite lubricant before each pour.

Needs: A protective coating that can withstand molten-aluminum temperatures without coming off, and a method for preventing molten aluminum from wetting patterns and core pins.

R&D program envisioned: Develop/verify coating process .

NOTE: Complex geometry is a special problem, e.g., transmission cases.

Time scale: Process could be used immediately. R&D program could require ≈ 3 years.

Payoff: Several industries have this problem. Some patterns cost up to $750,000. Doubling life of patterns would produce large dollar savings and result in significantly enhanced international competitiveness for U.S. manufacturing industries.

S. Wear Life of Large Ferrous Metal-Forming Dies

Problem: Large ferrous metal-forming dies used in current production break down, resulting in costly downtime for repairs, scrap, and sometimes poor quality. Only a limited number of cost-effective processes are available to improve the wear life of large dies.

Current approach: Ion-(plasma) nitriding, hard-chrome plating, and flame-hardening.

Needs: Other surface processing should accomplish the following:

- Improve tool life a minimum of two times.
- Be repairable.
- Be cost effective to apply.
- Be applicable to current tool materials.
- Preferably be a "visual" process.

Time scale: Needed immediately. R&D program might require 2-3 years.

Payoff: Reduced tooling costs, improved part quality, and improved competitive position for all of U.S. stamping industries.

T. Modeling of Surface-Coated Wear Materials and Adhesive Coatings

Problem: Modeling of wear of surface-coated materials and adhesion mechanisms of coatings is inadequate for guiding future developments.

Current approach: Empirical experimental methods, which are unreliable for quantitative understanding of adhesion or for predicting wear rates of coatings under various application conditions, including particle erosive wear.

Needs: Accurate modeling methods and properties of coatings (especially adhesion strengths).

R&D program envisioned: Methods are needed to measure properties of surface coatings and adhesion strengths of coatings to various substrates. Mechanisms of coating failure need to be developed at both low and high temperatures. These results should be incorporated into a readily accessible tribology data base such as ACTIS and would serve as the basis for reasonable model development.

Time scale: 3-5 years.

Payoff: Ability to predict component life and forestall premature failures.

23. POLYMER-METAL(OXIDE) INTERFACES

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I. INTRODUCTION

Some of the primary objectives of surface processing are to produce strong bonds between adhesives or coatings and substrates, to enhance the durability of bonds during exposure to service environments, and to improve the reliability of technologies that involve surface phenomena. These objectives must be achieved while improving the recyclability of products and reducing costs and environmental concerns.

The end product of many surface processes is an interface between dissimilar materials. These interfaces occur throughout the transportation and renewable energy fields and are becoming increasingly important as performance and lifetime requirements increase. In this paper, we review the needs and opportunities for technological advances involving interfaces and interphases—the transition zone around an interface (from a few atomic or molecular dimensions to many thousands) where material properties differ from those in the bulk. Our initial charter focused on metal(oxide)-polymer interfaces. However, our deliberations have been intentionally general so that they could also include polymer-polymer or ceramic-polymer interphases and are not specific as to which material is considered the substrate and which is considered the overlayer. In a particular study, the materials and/or processes must be specified, but our recommendations are not restricted to a given system.

Interphases are important because they control the performance of adhesive joints, composites, and coatings. In adhesive joints and composites, stresses are transferred across the interphase. Formation of an interphase that is mechanically weak or is vulnerable to environmental attack will result in a composite or adhesive joint that has poor properties or a short lifetime in service. Coatings protect against corrosion of substrates. If the interphase has poor mechanical properties or is susceptible to environmental degradation, delamination of the coating will occur, resulting in loss of corrosion protection for the substrate.

Interphases between polymers and metal(oxides), ceramics, and other polymers are found in several broad classes of applications listed in Table 1. We identified several generic challenges and problems facing industry today that can impede product and process improvements (see Table 2).

The initial stage of a new or modified product or process involves design. Among other things, it is essential to know how the different materials involved interact with each other: Will an adhesive or coating wet the substrate? Will the two materials adversely react with each other to degrade the interphase? Do the two materials forming an interphase have different coefficients of thermal expansion (CTEs) that will result in interfacial stresses during thermal cycling? Will a secondary material, such as a mold release or unintentional contaminant, find its way to a bonding surface and degrade the interphase?

Table 1. Sources or Applications of Polymer-Metal(Oxide), Ceramic, or Polymer Interphases

Painted metals or plastics
Adhesively bonded structures
Composites
Encapsulants or sealants
Metallized plastics
Microelectronic devices
Sensors

Lifetime requirements for products are increasing. To reduce life-cycle costs and support warranty policies, accurate lifetime projections based on short-term accelerated aging tests are needed as discussed in Chapter 25.

Fabrication of a component is the next stage in its life cycle. For large-scale production in either the transportation or renewable energy field, the process must be cost effective. A process that is labor- or time-intensive might be acceptable for production of hundreds of multimillion dollar airplanes, but not feasible for millions of multithousand dollar automobiles. Similarly, commercially feasible terrestrial photovoltaics need much lower production costs than those intended for spacecraft. Process tolerance is related to cost effectiveness. Stringent process controls and quality rejected components are expensive. Conversely, broad acceptable windows for process variables allow process variability without affecting quality. As environmental restrictions become tighter, processes involving environmentally hazardous materials will become more costly, if not disallowed. Chlorofluorocarbons (CFCs) are scheduled to be phased out over the next several years, and disposal of chromates and other toxic materials will become more difficult and expensive. Alternatives to process steps involving such materials must be developed.

At the other end of a product's lifetime, recyclability is becoming a more important issue. There will be increasing needs and requirements to recycle used automobiles and other products into new items to conserve limited resources and to reduce disposal needs.

Table 2. Challenges and Problems: Polymer-Metal(Oxide) Interfaces

Design (system/material compatibility, lifetime predictions)
Processibility (cost effectiveness, tolerance to produces variations, environmental acceptability, recyclability)
Performance (durability, strength, toughness)

Performance of a component is probably the most straightforward of the items in Table I. Initial properties are relatively easy to obtain and test. Durability, especially for components exposed to moisture, is generally more difficult to achieve and to predict qualitatively, as discussed above.

Research Needed:

To address these challenges and problems, we have identified seven technology areas in which there are research needs and opportunities (Table 3). Each of these areas is discussed in detail below. Two areas (characterization and accelerated testing) are covered in Chapters 25 and 26; here we emphasize their application for metal(oxide)-polymer interphases.

The identified areas include basic studies in which advances in fundamental understanding are needed to foster technological advances. More applied process improvements involving surface treatments and polymer coating/formation methods will allow cost savings, reduction in environmental burdens, and/or increased performance and reliability. Finally, process tolerance is specific to individual cases, but understanding of process sensitivity is critical for product reliability and can directly affect costs.

II. INTERPHASE FORMATION MECHANISMS

To achieve the goals discussed above, new or improved surface processes must be developed from a fundamental knowledge of how interfaces are formed between dissimilar materials. Polymer/metal (oxide) interphases form for many reasons. Metal surfaces are covered by a layer of oxide in which the oxidation state of the metal ions may differ as a function of distance from the metal. The outermost surface of the oxide may be covered by a layer of hydroxide and by several layers of adsorbed water.

Table 3. Prioritization of Research Needs (C, Crucial; I, Important; U, Useful)

Technology Areas	Fundamental Research	Applied R&D
1. Interphase Formation Mechanisms	I	U
2. Interphase Degradation Mechanisms	C	I
3. Characterization		
a. Surface	I	U
b. Interphase	C	I
c. In-process monitoring	C	C
4. Surface Treatments	U	I
5. Polymer Coating/Formation Methods	U	I
6. Testing		
a. Adhesion measurements	U	I
b. Accelerated aging testing	I	I
7. Process Tolerances	U	C

Polymer systems may contain polymer molecules with variations in chemical composition (copolymers and blends) and in physical structure (branches, isomers, molecular weight, and stereoregularity). They may also contain low-molecular-weight organic compounds such as curing agents, catalysts, accelerators, lubricants, plasticizers, coupling agents, antioxidants, and ultraviolet (UV) stabilizers as well as inorganic fillers.

All of these factors contribute to the formation of polymer/metal interphases. Low-molecular-weight polymeric or nonpolymeric molecules may segregate to the surface of a polymer so as to lower the surface energy. High-molecular-weight polymer molecules may be preferentially adsorbed onto a substrate. Low-molecular-weight nonpolymeric components may segregate to the interphase because of incompatibility with the bulk polymer. If a low-molecular-weight compound segregates to the interphase, it may react with the oxide, resulting in reaction products that may accumulate at the interface or diffuse into the polymer. Polymer molecules may be adsorbed onto metal(oxide) substrates through reactive functional groups. This will result in a lower state of cure at the interphase than in the bulk polymer. Sputtering of metallic ions from the oxide may occur during plasma polymerization on metal(oxide) substrates.

In the case of polymer/metal(oxide) interphases, it is essential to determine the surface chemistry of the substrate. This includes determining the oxidation state of metal ions in the oxide, the way in which the oxidation state of the metal changes as a function of depth below the surface, and the presence of hydroxyl groups and water molecules on the outermost surface of the substrate. The nature and extent of surface contaminants is especially important.

It is also essential to thoroughly characterize the polymer. This includes determining structural characteristics of the polymer such as stereoregularity, isomerism, molecular weight distribution, comonomers, and branches. It also includes determining the presence of low-molecular-weight additives such as curing agents, catalysts, accelerators, lubricants, plasticizers, coupling agents, antioxidants, and UV stabilizers.

Mechanisms by which complex polymer systems interact with (oxidized) metal substrates must be determined. This includes determining the extent of preferential adsorption of high-molecular-weight polymers onto oxidized metal substrates and the segregation of low-molecular-weight nonpolymeric components to the interphase. It also involves determining the effect of structural variables such as branches, stereoregularity, molecular weight, and isomerization and the effect of chemical variations, such as comonomers, on preferential adsorption.

We need to determine the nature of reactions between components of polymer systems and metal oxides. We specifically need to determine the extent to which oxides are etched, the nature of organometallic compounds that are formed, the extent to which the organometallic compounds accumulate near the interface or diffuse into the bulk polymer, the solubility of the compounds, and the extent to which these compounds inhibit cure of the polymer. It is especially important to determine the rates at which these various processes occur.

It is imperative to determine how processing affects the structure and properties of interphases. When a polymer is deposited onto a substrate, processing variables such as the solvent in which the polymer is dissolved, the rate at which the solvent is removed, and the cure temperature of the polymer may have a profound effect on the structure and properties of the interphase. In some cases, a similar polymer may be deposited on a substrate by several very different processes. For example, a polyimide may be deposited onto a substrate by spin-coating a solution of polyamic acid onto the substrate from solution and then thermally curing the polyamic acid or by vapor-depositing appropriate monomers onto a substrate to obtain the polyimide. It is reasonable to assume that the molecular structure of the interphase and thus its properties are very different in such cases, but little progress has been made in identifying the differences and determining their effects on the properties of the films.

In some cases, such as plasma polymerization, the polymer is not formed until the coating operation is carried out. In those cases, the polymer cannot be characterized prior to deposition. It is then essential to determine the molecular structure of the as-deposited coating. Characteristics such as chemical bonding between monomers to form polymers, orientation of polymer molecules, preferential sputtering of metal ions from oxide, extent of thinning of the oxide, and formation and solubility of organometallic compounds in the film must be determined.

In the case of metal/polymer interphases, it is essential to determine the extent of surface segregation by low-molecular-weight polymeric or nonpolymeric components and the way in which metals interact with those components.

Research Required:

To understand how interphases are formed and then use this information to improve processing and products, the following research is needed:

- Characterization of both the substrate surface and the overlayer
- Identification of the mechanisms by which the polymer interacts with the substrate and the changes induced by these reactions
- Determination of the rates at which these reactions occur
- Determination of how processing affects the structure and properties of the interphase.

III. MECHANISMS OF DEGRADATION

Interphase degradation is an issue affecting all polymeric interphase systems (polymer/metal, polymer/metal oxide, and polymer/polymer). Degradation is discussed, in general, in Chapter 25; here we concentrate on degradation of interphases. To design more durable systems, a phenomenological and mechanistic understanding of the processes involved in degradation is necessary. To achieve this goal, the following approach should be considered:

> Characterization of the interphase chemistry as a function of environments leading to degradation of the system.
>
> Determination of the kinetics and comparison of the extent of degradation to the time of exposure.
>
> Correlation of interphase modification/degradation to performance.

Historically, the effect of moisture has been considered the major factor resulting in decreased system performance. The influence of water initially present and diffusing to the interphase region has been studied comprehensively on a variety of systems. However, as new materials are developed (especially regarding polymer/polymer interphases), new avenues for significant research exist.

Comparison of different polymer chemistries to their inherent susceptibility to interphase water infusion should be correlated to performance. In addition, performance of various polymer chemistries should be correlated to water initially present at the interphase. To achieve this, quantitation of diffusion rates and amount of water present at the interfaces should be determined. The resultant interphase chemistry should be related to performance. Finally, the effects of water are sometimes very localized due to clustering, necessitating the use of spatially resolved analytical techniques to investigate this phenomenon. The results of this type of study can be directly related to process studies by relating this information to the moisture environment occurring in the manufacturing of these materials.

Research should also be initiated exploring the effects of other fluids on the performance of polymer interphase systems. A research approach similar to that discussed in the previous section can be easily applied to other fluid and gas-induced degradation mechanisms. The "other fluids and gases" that should be studied are those present in the manufacturing environment, process chemistries, or service environment. Two specific examples of research needs in this area are: (1) Solvent compatibility to materials in polymer/polymer interfaces, specifically polymers on plastic substrates, are generally unknown. What is the effect of solvents on the interfacial chemistry and resulting performance? (2) Conformal coatings on sensors and electronic devices are designed to protect these materials from various "harsh" environments in automotive applications. What influence do various fuel formulations and exhaust chemistries have on the interphase chemistry and, in turn, long durability of the interphase?

It has been established for quite some time that the fundamentals of corrosion in polymer/metal (oxide) systems are based on ionic reactions. Heterogeneous redox reactions at the polymer/metal(oxide) interphase occur as the metal is oxidized and the polymer system is reduced. Both anodic and cathodic processes can occur in these systems. In order for these reactions to occur, water must be present within the system, primarily at the interface. The effects of water and research needs pertaining to this subject have already been addressed. Ionic corrosion processes are of paramount concern to the transportation industry, because they are the quintessential factors that govern the corrosion life of vehicle bodies. Extensive research has been accomplished in the study of polymer/steel systems; however, as new polymer formulations and steel surface treatments are developed, this work should be continued. In addition, as various industries incorporate a greater amount of adhesive bonding into their products, bonding of dissimilar metals presents new challenges in corrosion research. Dissimilar chemistries of electrically connected materials form galvanic couples and generally accelerate the ionic reactions occurring within the system. A systematic approach to ionic-contributing degradation, similar to that proposed in the section dealing with moisture-induced degradation is needed. The effects of residual ionic content as well as diffusion of ionic species resulting from environmental exposure need to be addressed.

Numerous studies have been reported concerning UV degradation of polymer and polymer interfacial systems. This area remains of key interest to a number of industries. The incorporation of "light stabilizers" has reduced many of the deleterious effects of UV exposure but has resulted in problems of its own relating to stabilizer segregation and actual alteration of interfacial chemistry resulting in reduced system performance. Indeed, the extent of degradation is dependent on the film thickness. Therefore, research can be focused on blocking and reducing the effect of UV exposure through various additives, modifications, and novel polymer formulations.

Radiation-induced degradation resulting from exposure to electric fields is another area that needs additional research. Although this type of radiation is not as great a concern at this time as UV degradation, the effects have very serious implications to both the energy and transportation industries. These effects have not been well characterized, and a systematic approach to characterize the long-term issues is necessary.

The chemistry of the interphase region is highly dependent on temperature considerations. Cure temperature and service temperature of polymer-related interphases can alter these interfacial chemistries. Differing temperature schemes result in segregation of additives and components that may affect system performance. This is increasingly evident in polymer/polymer interphases (such as paint on plastics) in which there may be a great difference in cure temperatures of the different paint layers and the plastics. The result is interphase segregation of aforementioned components in the system as well as substantial changes in interphase chemistry. This reveals a relatively untouched field of research that needs to be addressed.

Another area of research that needs to be addressed is the adhesive bonding of dissimilar substrates. When bonding substrates with dissimilar heat capacities to be used in a harsh service environment, such as automotive applications, the temperature differential may cause alteration/degradation of the interphase chemistry. Long-term durability and system performance as a function of substrate temperature disparities in adhesive bonding is an area of research that is relatively unaddressed at this time. More well understood is the effect of substrates having different CTEs. If the adhesive is not compliant enough to handle the strains induced as the dimensions of one substrate change with respect to the other, delamination and bond failure can occur. Improved means to prevent such delamination are also needed.

The degradation of polymer-related interphases can be highly dependent on mechanical factors such as strain and stress. Although normally the interphase chemistries are not modified by these factors, the adhesion performance and durability of polymer systems may be greatly affected. In many cases, the durability will depend on the timing of a load, i.e., a cyclic stress will generally cause bond failure at lower levels than a continuous stress. Coating and adhesive industries have given considerable attention to these influences in the past and addressed these issues as mainly an engineering problem. In the scope of this work, research in the degradation mechanisms should consider what changes in mechanical attributes such as strain and stress are experienced after interphase degradation induced by these mechanisms.

Research Required:

Many aspects of the degradation of interphases are not yet understood. The most important of these are listed below.

- Establishment of interphase degradation mechanisms in typical service environments that include moisture, ionic solutions and other fluids, radiation, stress, and temperature.

- Determination of synergistic effects (positive or negative) between different components that affect either the mechanisms or rates of degradation

- Development of means to retard interphase degradation.

IV. INTERPHASE CHARACTERIZATION TECHNIQUES

All aspects of understanding, engineering, and manufacturing of solid/solid interphases require the ability to measure the composition, chemical bonding, and structure of the components of the interphase in all three spatial dimensions. How the composition, bonding, and structure of the interphase change with time can give insight into the mechanism of interphase formation, the role of surface treatments and impurities, information on how interphases degrade, and the effects of processing parameters.

Unfortunately, current techniques generally permit only limited studies of model systems or postmortem analysis of failed interphases. Methods to monitor the formation of interphases during actual manufacture do not exist. Thus, research into analytical techniques should emphasize nondestructive determination of interphase composition and chemistry, surface characterization in ambient environments in real time with high spatial resolution, and monitoring of interphases during manufacturing. The background and research needs for surface and interphase characterization are discussed in more detail in Chapters 1, 3-7, and 26. Here we emphasize the needs concerning metal(oxide)/polymer interphases (Table 4).

Current methods to analyze interphases can be loosely divided into two categories, destructive and nondestructive. Destructive methods usually utilize traditional surface analysis techniques, after ion sputtering to the interphase, eroding away the overlayers or causing the interphase to fail mechanically (e.g., peeling or fracturing). Traditional surface analytical techniques achieve their utility due to the limited penetration length of the probe, either ions or electrons. As a result, these methods require that the overlayer be removed so that the interphase can be studied. Correlation between the mechanical force to cause the joint to fail and observations of the interphase provide useful postmortem information. However, the process of destroying the interphase to analyze it always complicates the interpretation of the results.

Nondestructive techniques to analyze interphases must utilize probes that have long penetration depths. It is the conflict between the long penetration depths of the probes and the limited thickness of the interphase that makes development and improvement of these techniques difficult. Despite their long penetration depths, these techniques recognize the uniqueness of the interphase, either through the breakdown in symmetry between two isotropic phases or some unique elemental composition at the interphase. Certain optical spectroscopic techniques such as second harmonic generation (SHG) and sum frequency generation (SFG) can be used to study interphases between two isotropic (centrosymmetric) media. At this interphase, two photons of either the same or different energies can be converted to one photon with the energy equal to the sum of both incident photons. Changes in the SHG or SFG signal can be related to changes in the interphase, e.g., changes in the vibrational spectrum or changes in the symmetry of the adsorbate. Surface-enhanced Raman spectroscopy (SERS) uses the enhancement of the vibrational Raman spectrum in the vicinity of a rough silver, gold, or copper surface to provide distinct

Table 4. Selected Techniques for Interphase Characterization

- Destructive methods using conventional surface analysis
    - Ion sputtering
    - Abrasion
    - Peel/Fracture
- Nondestructive methods
    - Second harmonic generation (SHG)
    - Sum frequency generation (SFG)
    - Surface-enhanced Raman spectroscopy (SERS)
- Composition-specific methods
    - Mossbauer spectroscopy
    - X-ray absorption near edge structure (XANES)
    - Extended X-ray absorption spectroscopy (EXAFS)
- Liquid and ambient environment methods
    - Electrochemical impedance spectroscopy (EIS)
    - Fourier transform infrared spectroscopy (FTIR)
    - Near infrared spectroscopy (NIR)
    - Spectroscopic ellipsometry (SE)
    - Differentially pumped scanning electron microscopy (SEM)
- Process monitoring techniques
    - Optically stimulated electron emission (OSEE)
    - X-ray or ultraviolet fluorescence
    - Dielectrics
    - Surface reflectivity

chemical information concerning organic layers over these metals. Although the use of optical spectroscopies to probe buried interphases is in its infancy and only well-characterized model systems have been studied, their promising results warrant more future investigation.

Certain other techniques can take advantage of long penetration depths typical of bulk analyses and make them sensitive to the interphase. For example, the interphase can be made compositionally unique. Work has shown that Mossbauer spectroscopy can be used to study the delamination of paint from steel if the steel surface is isotopically enriched before painting. Unfortunately, Mossbauer spectroscopy is limited to systems containing tin, iron, or a few other elements. X-ray absorption techniques have shown promise when a thin (approximately 100 Å) layer of metal has a polymer adsorbed on it or is adsorbed on the polymer. Details in the X-ray absorption edge and the X-ray absorption near edge structure (XANES) can yield information about the electronic structure of the metal. Similarly, extended X-ray absorption fine structure (EXAFS) can help describe the local structure around the metal atoms. If the X rays are energetic enough (the transitions deep enough), these analyses can be performed in air. Unfortunately, analysis of C, N, and O is difficult because the penetration depth of these characteristic X-rays is small. All of these X-ray techniques require the use of a synchrotron to get an intense source of variable energy X rays.

Certain electrochemical techniques, such as electrochemical impedance spectroscopy, are themselves techniques to study solid/liquid interphases and have been used to examine corrosion at polymer/metal interphases. Undoubtedly other bulk techniques can be identified and adapted for the analysis of interphases. Vacuum surface analysis techniques such as electron and ion spectroscopies (Chapter 1) are mature and can provide compositional and bonding information in two dimensions. However, sample preparation and the vacuum exposure may change the surface properties and may impede the observation of specific effects as a function of time, i.e., contamination, surface processing reactions. Thus, it is important to develop surface analytical techniques that can work in ambient environments in real time to determine the composition, morphology/structure, and/or chemistry of the surface. In some cases, such as microelectronics, high spatial resolution will also be needed. Many of the techniques described above for analysis of solid/solid interphases will apply here, but the constraints differ. Some specific examples of techniques are Fourier transform infrared (FTIR) spectroscopy, near infrared (IR), spectroscopic ellipsometry (SE), and scanning electron microscopy (SEM) operating with the sample under a partial vacuum, but with a combination of skimmers and differential pumping to reduce the pressure in the microscope column. Development of techniques like these will have two immediate advantages: understanding the effects of surface processing and developing process monitors.

The development of process monitors is a neglected area. These monitors provide real-time information about the cleanliness of a surface, the coverage or thickness of an overlayer, the degree of cure of an adhesive, or the composition or chemistry of a reagent. Such monitors have to be simple to use and robust, and must yield unambiguous results. Often simple techniques, such as surface reflectivity, light scattering from particles, or optical density can be adapted to the manufacturing environment. Other techniques such as optically stimulated emission (OSEE), X-ray or UV fluorescence, and dielectrics have been successful in monitoring a system and providing real-time information. However, in each case, limitations of the techniques prevent routine, general use. As with the more sophisticated analytical methods proposed above, their use might also be extended. As process monitors come into more common use, better process control will result in more reliable and higher performance products.

Research Required:

Increased understanding of polymer-metal(oxide) interphases and improvements in their performance require that they be well characterized. Characterization needs include:

- Development of techniques capable of investigating buried interphases nondestructively.
- Improvement of methods to probe solid/liquid interphases in situ.
- Development of process monitors capable of examining surfaces and interphases in ambient production environments and providing real-time analysis for feedback control.

V. SURFACE TREATMENTS

Surface modification or treatment of a substrate is commonly needed in order to obtain good adhesion of a coating to the substrate. These treatments are intended to clean the substrate, remove undesirable material (weak boundary layers), introduce desirable chemical functionalities into the surface, and render the interphase water-resistant.

The optimum surface treatment depends on the nature of the substrate and coating material, the process used to deposit the coating, environmental considerations, and the conditions under which the coating-substrate combination will be used. For example, different treatments are effective for inorganic (metal, oxide) surfaces than for organic (polymeric) substrates. Furthermore, the whole area of surface treatments can be divided into two categories, one in which the surface is superficially modified (e.g., a chemical etch) and one in which a discrete layer of desired material is intentionally deposited (e.g., use of a conversion coating or an adhesion promoting layer). Also it should be emphasized here that these treatments can be wet or dry, vacuum or nonvacuum, simple or complex. Many surface treatments are available (see Table 5), and there is considerable interest in improving the existing ones or devising new and improved ways to modify surfaces.

Considerable cost is frequently expended in modifying metals and other inorganic substrates for bonding purposes, so the need for a desirable surface treatment for such inorganic substrates is quite obvious. There is also a strong trend in the automotive industry toward using increased amounts of

Table 5. Classes and Examples of Surface Treatments

- Chemical
    - Chemical reactions (oxidation, sulfonation, ozonation, and phosphatization)
    - Etching
    - Deposition/adsorption (LB films, coupling agents, and corrosion/hydration inhibitors)
    - Photochemical
- Physical (plasma, UV, X-ray, laser, and ion bombardment)
- Mechanical (abrasion, casting against other materials, and surface texturing e.g., lithography)
- Metallurgical (cladding)

plastics, which pose special requirements and challenges for adhesive bonding. Some of the needs and challenges are listed below:

> Treatments should be environmentally acceptable. In the future, strict regulations will be imposed with respect to disposal of chemicals and recycling treated materials. Surface treatments should pose minimal disposal problems, and treated materials should be recyclable.
>
> The effects of surface treatment should persist over a period of time. It should be possible to treat the surface of a material, store or transport the material, and use the material later without the surface treatment losing effectiveness. For example, the effects of plasma surface modification are lost after a period of time, but the time depends on a number of factors.
>
> Surface treatments should be fast, cost-effective, simple to perform, and applicable to large, irregularly shaped parts.
>
> Treatments should be compatible with the mode of deposition of the coating and processing conditions involved.
>
> Surface treatments should improve both dry and wet adhesion. They should also render the bond durable over the life of the coating.

Research Required:

Research efforts should be directed toward exploring alternative surface modification techniques/processes to supplement or replace those that currently exist but have certain inherent negative traits. More specifically, research should be directed toward:

- Determination of the characteristics and properties of surfaces before and after treatment
- Evaluation of the effectiveness of various surface treatment techniques
- Establishment of the mechanisms and kinetics by which the effectiveness of a treatment is degraded
- Identification of the mechanisms and optimization of new techniques for surface modification
    - UV sensitization
    - plasma surface modification
    - laser surface treatment
    - surface modification by microorganisms
    - self-assembled monolayers
- Determination of the effects of surface modification by adhesion promoters and the mechanisms by which adhesion promoters deposited by different methods function.

VI. NEW METHODS FOR POLYMER DEPOSITION

To tailor interphases for specific applications, it is necessary to develop new methods for depositing polymeric films on metal, ceramic, semiconductor, or polymer substrates. Plasma polymerization is an extremely attractive technique for such purposes.

A. Plasma Polymerization

Plasma polymerization refers to the vacuum deposition and polymerization process that utilizes reactive species created in a plasma state and the surface bound reactive species created by the interaction of the surface exposed to the plasma state. Plasma polymerization has many advantages over conventional methods of coating or film application. One unique advantage of the technique is its capability for creating compositionally and structurally graded interphases that bridge two distinctly different materials. Adhesion of plasma polymerized coatings to substrates is usually outstanding. Since deposition and polymerization occur simultaneously, a film deposited on an organic polymer substrate is essentially covalently bonded. Although adhesion to an inorganic substrate (metal, ceramic, and glass) by covalent bonds is unlikely, tenacious adhesion to such substrates can often be obtained by virtue of interphase atomic mixing.

In plasma polymerization, the deposition and polymerization processes are combined so that the problem of nonwetting of the substrate by the coating or coating solution is eliminated. Plasma polymerization is a dry process that does not require the use of solvents. Consequently, the process yields minimal effluents, and the products contain few volatile organic compounds.

Plasma polymerization is usually carried out in a closed environment (vacuum, reduced pressure, or sealed environment) and can thus be combined with other important processes such as cleaning, etching, oxidation or reduction of the surface, and functionalization of the surface, into essentially one operational step. Polymers can be deposited without exposing the cleaned or modified surface to the atmosphere, thus reducing the chance of recontamination or inadvertent chemical reactions such as oxidation. Furthermore, polymers prepared by plasma polymerization have significantly different molecular structures than conventional polymers, which are prepared from the same monomers and applied from solution or the melt. Most plasma polymers are extensively cross-linked and are thus insoluble and infusible and have outstanding barrier characteristics.

B. Other Vacuum Deposition Techniques

Although plasma polymerization is a very important alternative to conventional solution techniques for deposition of polymer films, other techniques, such as parylene polymerization, in which thermal decomposition of dimers of para-xylylene derivatives is utilized to deposit a film on a substrate, and vapor deposition polymerization, in which monomers are adsorbed onto a substrate and thermally polymerized, are also promising processes. In parylene polymerization, a discrete, well-defined reactive species is created by thermal cracking of the starting material (dimer). The mechanism of deposition and polymerization is believed to be similar to that in plasma polymerization. Because of the well-defined chemical structure of the reactive species, the resulting polymers are semicrystalline (in contrast to plasma polymers, which are amorphous), and contain linear segments of considerable length. Due to topographical crosslinking, as-deposited polymers are insoluble and infusible in most cases. Because of their semicrystalline nature and the presence of crosslinks, the polymers have excellent dimensional stability and chemical resistance.

The reactive species have a specific reactivity toward similar chemical structures. Consequently, adhesion of parylene films to many surfaces is poor. The lack of chemical bonding to a substrate can be overcome by plasma pretreatment or deposition of a plasma polymer onto an inorganic substrate (metal, ceramic, glass, and semiconductor). By comparison, parylene deposition results in films that have an exceptionally high degree of penetration into small spaces and excellent mechanical anchoring to porous substrates.

In vapor deposition polymerization, monomers are adsorbed onto a substrate where they react to form a polymer film or an intermediate, which is then polymerized thermally. This technique, which has been applied to polyimides and polyamides, does not require the use of solvents. Thus, vapor deposition polymerization enables health and safety problems associated with solvents used to cast polymer films to be eliminated. It also enables problems related to solvents entrapped within solution-cast polymer films to be eliminated. However, vapor deposition polymerization can result in films having molecular structures that are considerably different from those of films obtained by casting polymers from solution onto substrates.

Research Required:

Research on plasma polymerization and vapor-deposition polymerization should be directed toward:

- Development of new methodologies of plasma polymerization to improve:
  - Distribution of polymer deposition on a large surface
  - Deposition in recessed areas
  - Adhesion and passivation of surface
  - Modification of polymeric substrates without degradation
- Development of low-temperature plasma torches that can be used in robotic spray coating
- Establishment of robotic operation in vacuum
- Determination of the effects of processing variables on the molecular structure and properties of vapor-deposited films
- Comparison of the structure and properties of vapor-deposited polymer films to those of solvent-cast films.

VII. TESTING

Adhesive bond strengths are commonly measured by tests such as lap shear, peel, T-peel, climbing drum, button pull, etc., depending on the materials and the anticipated stresses on the bonded component. Several variations of each test have been developed and for many applications, these tests are well established and adequate. However, these tests do not provide information in two areas of interest: interphase bond strength and nondestructive bond testing. While the interphase bond strength plays a factor in all the tests mentioned above, energy dissipation within the bonded materials as they deform also contributes to the measured value and, in many cases, can dominate the measurements. To improve our understanding of interphase formation and degradation mechanisms, a means to measure and/or predict interphase bond strength based on the chemical and physical bonding occurring at the interphase is needed. Such knowledge would allow improvements and optimization in bond performance from first principles instead of the empirical approach currently used.

In the best of worlds, a means to measure bond strength without disrupting the bond would be of great advantage—actual bonded components could be tested prior to being placed into service to assure bond performance. The state of the art of testing will need significant improvements before such inspection becomes possible. A more feasible, but not currently possible, inspection would be the detection of weak and kissing unbonds in which the two materials are in intimate contact with each other, but whose bond will not allow significant transfer of stresses from one to the other. Current nondestructive evaluation (NDE) techniques, such as ultrasound, radiography, eddy current, and thermography, rely on a separation between two materials and detect the gap between them. Weak and kissing unbonds do not have a gap and, hence, are not detected until they separate. If this happens during service, failure of the bonded component may occur. Detection of weak and kissing unbonds in the production facility would increase reliability of the component and potentially could allow weight, size, or cost improvements as product variability is decreased.

The projected lifetime of a bonded structure or the durability of an adhesive joint is commonly determined using accelerated aging tests. For most components, lifetime requirements are too great and material/process advances too rapid to allow real-time testing. Several accelerated tests are available to allow real-time testing. These are discussed in another chapter and will not be reviewed here. Rather, we will briefly present some of the issues pertinent to polymer-metal(oxide) interphases.

The key potential danger in an accelerated test is that the degradation mechanisms will differ from those experienced in the service environment. A classic example is an egg—if a hen incubates her egg for 21 days at 103°F, a chick results, but if the same egg is placed in boiling water for 10 minutes at 212°F, a hard-boiled egg results. Thus, it is crucial to ensure that the degradation mechanisms in the service environment and in the accelerated test are similar.

Screening tests of materials are perhaps the simplest types of tests. As a system is fabricated and becomes more complicated, test conditions become more critical. Does one component affect the degradation of another? An example of a beneficial effect would be paint reducing the degradation of the metal substrate; an example of a detrimental effect could be road salt reacting with the galvanized steel in a car to deteriorate nylon fuel lines.

The configuration of a part can lead to locally severe environments under typical service conditions. Crevices or cracks where moisture can accumulate provide a more severe local environment than a vertical flat surface where water runs off. Stresses experienced by one part must also be considered as part of the overall environment. In general, a stressed component will fail before an unstressed component, and a cyclically stressed component will fail before a statically stressed one.

Improvements in the ability to rapidly determine relative lifetime ranking of components would be a valuable but incremental advance in technology. The ability to accurately determine the (minimum) lifetime of a structure would be a major advance in technology for a wide range of industries.

Research Required:

The research needs in accelerated testing are presented in more detail in chapter 25. From the perspective of polymer-metal(oxide) interphases, the testing needs include:

- Development of methods to measure interphase bond strength or toughness with contributions from the bulk materials.
- Development of methods to nondestructively measure bond strength or, at least, detect weak and kissing unbonds
- Development of methods that accelerate the aging of an interphase without changing the degradation mechanisms
- Establishment of a means to determine the acceleration factor of a test.

VIII. UNDERSTANDING EFFECTS OF PROCESS VARIABLES ON INTERPHASE PROPERTIES

Processing variables commonly control the physical and chemical properties of an interphase and, hence, the performance of a structure. Interests in processing have both basic and applied aspects. From a fundamental point of view, a process controls how an interphase is formed. When a polymer is deposited onto a substrate, processing variables such as the solvent in which the polymer is dissolved, the rate at which the solvent is removed, and the curing temperature of the polymer can have a profound effect on the structure and properties of the interphase. In some cases, as we have seen, similar polymers may be deposited on a substrate by several very different processes. It is reasonable to assume that the molecular structure of the interphase and thus its properties are very different in such cases, but little progress has been made in identifying the differences and determining their effects on the properties of the films.

From a manufacturing point of view, processing is the key to production. Processing governs the performance of the system, its reliability, and its cost. Knowing how changes in a processing step or a processing variable affects each of these, allows an engineer to optimize the process for a particular application. Major factors determining the fabrication cost and the capability to manufacture a part are the limitations for each process variable; a process that requires stringent controls on a process variable will be more expensive than a tolerant process. Table 6 lists some of the parameters that might need to be monitored to ensure adequate control of the process.

Table 6. Process Parameters with Potential Monitoring Needs

Substrate cleanliness	Moisture content
Degree of cure	Solid/vehicle ratio
Thickness	Appearance (gloss/color)
Uniformity	Solution pH
Viscosity	Material contamination
Mix ratio	

Inevitably, there will be instances when the process falls outside the process window. In most cases, when this occurs, the engineer has insufficient information for proper disposition of the part. Is the performance so degraded that the part must be scrapped? Is the resulting performance still adequate for use? Can the part be reworked to obtain adequate performance?

Historically, it has been common practice to establish the magnitude of process parameters empirically, and once the product attributes appear satisfactory, no further systematic studies are made to explore the limits and interactions of the process parameters. Thus it is not known if performance falls off dramatically at a certain point or if performance remains constant or slowly degrades as the process parameter varies further from specifications. Additionally, it is likely that process interactions depend on multiple variables so that an acceptable process window for one variable will depend on other variables. The empirical approach often results in unnecessarily rigid process specifications and often impacts the competitive capability of the product.

Optimum use of process windows once they are established involves process monitoring with active feedback control to control and verify that the process variables are within acceptable limits. Potential techniques and requirements for monitoring were discussed under characterization earlier in Section IV and in chapter 26 on surface characterization.

Research Required:

The ability to determine the strength and other mechanical properties of polymer-metal(oxide) interphases is critical to improvements in their performance. Some research needed in this area is

- Development of an understanding of how changes in processing affect interphase formation and degradation

- Development of an understanding of how process variables, either singularly or in concert, change the performance of a given system

- Development of the means to monitor the important variables and provide feedback to the process to optimize performance, reliability, and cost.

IX. SUMMARY AND CONCLUSIONS

Interphases between polymers and metals or their oxides, ceramics, and other polymers are commonplace in the transportation and renewable energy fields. The properties of these interphases can govern the performance of the structures and devices that contain them. We have identified several challenges and problems limiting improvements of these properties. Technology areas in which research is needed to advance interphase properties include: interphase formation and degradation mechanisms, interphase characterization, surface treatments, polymer coating/formation methods, testing, and process tolerance to variability. Each of these areas has been discussed in detail and prioritized with regard to fundamental research and applied research and development.

24. THE IMPACT OF SURFACE PROCESSING ON THE FABRICATION AND PERFORMANCE OF THIN-FILM, MULTILAYER SOLAR COLLECTORS

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I. INTRODUCTION

The purpose of this chapter is to provide a context for selecting research and development activities to achieve national goals in solar energy production. The details of these goals appear elsewhere [1]. Specific considerations in this session deal with issues in thin-film, multilayer solar collectors, which include photovoltaic (PV) solar cells, glazings, and reflector materials. Expanded descriptions of these components and goals for their development have been described previously [2-5].

The scope of our considerations encompasses the impact of surface processing on the fabrication and performance of encapsulated multilayer components for use in solar power generation and energy conservation. "Performance" is a generic term encompassing several figures of merit:

- Functionality (e.g., fill factor, efficiency for a solar cell)
- Cost
- Lifetime.

"Components" consist of two types:

- Electrically active = active (e.g., p-n junction)
- Electrically inactive = passive (e.g., mirror, encapsulant).

"Power generation" encompasses both the solar thermal and solar electric (PV) systems. Photochemical systems are described in Chapter 28 of this volume.

"Energy conservation" encompasses devices for thermal energy management [6].

The following sections describe the technical context, research strategy, and technology trends relevant to thin-film, multilayer solar collectors. Promising opportunities for the application of surface processing to the fabrication of multilayer devices are discussed next. Finally, a synopsis of the opportunities that exist in this technology area and typical examples are presented.

II. TECHNICAL CONTEXT

Active components (ACs) involve the photogeneration and electric field induced motion of charges. In a PV cell, the active components are those in which a photovoltage is induced by the absorption of light. This encompasses only a part of the total structure of the cell, as is illustrated in Fig. 1. In electrochromic devices, the active components are those that participate in electron ion motion and the associated changes in optical properties. These changes are induced by an external electric field. A representative device is illustrated in Fig. 2.

The passive components (PCs) we are concerned with include, among other items, mirrors, lenses, windows, and encapsulants. For PV arrays, PCs include the structural components of the modules themselves (Fig. 3). For mirrors, they include the flexible reflector films, but not the mechanical support structures (Fig. 4).

A central concept pertinent to the role of interfaces in active multicomponent structures is the profound effect of small amounts of trapped charge at these interfaces on device performance. For example, small amounts of corrosion at the metal-semiconductor contact may contribute a significant load to the cell, destroying its capability to meet design criteria (Fig. 5). Another example is the scavenging of ions in electrochromic windows by interfacial defects, which leads to a loss of optical switching (Fig. 6).

Multiple classes of pertinent phenomena in these systems are:

- Diffusion among contiguous layers (e.g., metal/semiconductor contacts), where diffusion barriers can be constructed
- Recombination centers at heterojunction interfaces in PV cells
- Grain boundary diffusion
- Ion trapping at interfaces in electrochromic cells.

A strong emphasis of our discussions was addressing how research could directly aid the development of engineering prototypes nearing commercialization. The critical issues affecting the future development of these technologies, including questions of design, materials selection, cost, and long-term performance, are well suited for designation as targets for basic and engineering research. We feel an overarching strategy for portions of this research program should be to identify the microscopic origin of macroscopic failure modes and, hence, surface processing means for mitigating these failures.

As for passive components, a central concept is to identify chemical (atomistic) phenomena that limit the life of the component (over times of the order of decades). The degradation is exacerbated by "hostile" environments (ultraviolet (UV), elevated temperature, O_2, H_2O, pollutants, soilants, hail, thermal cycles, etc.). For example, the PV module must be able to withstand the mechanical stresses of hail impact, and the optical surface must not be degraded by wind, soil, rain, and snow. Reflector materials and interfaces within them must not corrode over the service lifetime. Classes of pertinent phenomena are interdiffusion, mechanical damage (including residual stresses and installation damage), and chemical stability.

The research strategy is the same as for the active layers. The microscopic origin of macroscopic failure modes must be understood, and the fundamental limitations of choices of materials systems (glass versus polymer versus metal versus multilayer metal, etc.) must be determined so that the degradation mechanisms can be mitigated over the lifetime of interest.

Opportunities for improvement in both the active and passive components may exist as a result of recent progress in technology. Examples of such technical advances are the fabrication of superlattices, plasma-deposited network glasses (a-C), liquid crystalline polymers, and rapid thermal (surface specific) processes.

III. NEEDS AND OPPORTUNITIES FOR RESEARCH

A. Interface Modification

Perhaps the greatest opportunities for research lie in the general area of rational interface modification. The identification of specific component failure modes will often require modifications to be made that do not involve directly the bulk materials employed. Specific examples are presented in the areas of both active and passive components. PV devices can interact adversely with the metallization layers. Rational methods for modifying the metal-device contact are suggested by the hierarchical approaches now commonly employed in microelectronic device and multichip module assemblies. Significant opportunities exist for developing nonelementary multilayer metallizations that will improve lifecycle characteristics of the active components in a system architecture [6]. The design rules for PV systems are likely to be modest by the standards defined by microelectronics technologies and, as a result, considerable simplification may be possible that can help meet the cost constraints under which viable commercial technology must operate.

Assembled system architectures will likely involve numerous interfaces with polymeric materials (present either as structural and/or mechanical mediators, package constituents, and barrier layers) [3,4,5,7]. These latter materials are likely to be selected on the basis of bulk properties (e.g., resistance to gas permeation, viscoelastic properties, etc.). Significant improvement of the durability of multilayer architectures will require significant progress in improving the adhesion properties of the relevant interfaces [7]. Powerful methods are available for the rational modification of organic material interfaces with an objective of improving adhesion (this volume, Chapter 9). Gas plasma or chemical treatments are well-known methods in this regard. Microstructural modifications of materials interfaces by molecular self-assembly and adsorption methods also offer great promise for constructing thin interfacial layers of desired function and structure, layers imparting the desired adherent properties to heterogeneous interfaces without obviating the intrinsic advantages inherent in the bulk material properties (this volume, Chapters 17, 18, and 29). Indeed, an improved general understanding of adhesion in metal-organic, organic-inorganic, organic-organic, metal-metal, metal-inorganic, and other solid-solid interfaces is an area of considerable national need, having implications far beyond the specific technologies with which this report is explicitly concerned [7]. Surface processing and related sciences offer the potential of making dramatic contributions in these very important areas.

B. Patterned/Selective Deposition

Current methods of microelectronic device fabrication can be defined as being largely extractive; materials are deposited nonselectively and removed from areas where they are not wanted. Considerable process simplification and elimination of elements of the waste stream could be realized if cost-effective methods of selective deposition could be developed. These processes, once initiated, are chemically amplified by the complex mechanistic processes that define the reactive solid-ambient growth surface. The least expensive selective depositions currently use electroless plating (this volume, Chapter 10), a process typically limited to metals (e.g., Cu, Ni, and Ag). The specific requirements of a system architecture may require or be enhanced by depositions that can only be effected from the vapor phase. Surface processing concepts could powerfully enable process designs conceived around selective chemical depositions. Progress in this area will require that progress be made both in identifying novel chemical precursors, which cleanly and efficiently yield the desired solid phases, and in defining strategies that will effectively initiate their spatially defined deposition.

C. Electrochromic Windows

Electrochromic windows are active devices for effecting energy conservation and management [3]. Considerable progress has been achieved in devising suitable applications for such technologies in both buildings and transportation systems. Current designs for such systems, an example of which is shown in Fig. 7, have effectively negated any prospects for commercialization in less than 5 years. As shown in the figure, electrochromic windows are comprised of a multilayer thin-film architecture supported on architectural glass. The very aggressive electrolyte incorporated in this design suggests the considerable need existing to find better and safer materials for the construction of such devices. The myriad of interfaces that are present in such devices also suggest that considerable research effort is needed to understand the importance of interfacial properties in the performance and durability of these systems.

D. Novel Reflector Materials

Forming multilayer superlattices is a recent research area of potential importance for solar collectors. Superlattices have been widely studied for their unique electrical and mechanical properties. By fabricating multilayer metal films of suitable composition and thickness (e.g., alternating layers of a good reflector like Ag and reactive transition metals), it should be possible to generate highly reflecting films exhibiting exceptional mechanical and chemical stability.

E. Enhanced Stabilization of Polymeric Materials for Solar Energy Applications

Materials failures in the bulk can be accelerated by species derived from surface reactions. There are many well-known examples in which the dissolution of metal ions (the ions generated reactions with H_2O and O_2, for example) into a polymer can catalyze its decomposition in bulk [8]. Polymeric substrates, overcoats, and superstrates figure centrally in current high-performance, low-cost reflector designs [9]. The analysis of chemical reactions occurring at the buried interfaces presents a significant experimental challenge toward which research might reasonably be directed [10]. Additional research needs and opportunities at polymer/metal (oxide) interfaces are given in Chapter 23 of this volume.

F. Surface Processes of Active PV Components

One of the major issues that needs to be resolved in developing specific device properties is the control of electron-hole pair recombination velocities as a function of the device material processing. The presence of defects, either in the bulk or at the device interfaces, can provide trap sites that will diminish the electron-hole pair lifetime and decrease the carrier density. Although the problems of internal traps are best solved by the semiconductor growth processes optimized to control intrinsic lattice defects and impurity materials, the surface traps, because of the accessibility of the surface, exhibit the possibility of control by chemical removal. For example, surface traps on a GaAs (100) surface can be dramatically reduced by reaction with sulfide ions, and recent work indicates that reaction with organosulfur compounds offers additional possibilities [11]. Plasma treatments also provide passivation. Surface modifications are thus expected to make important contributions to the enhancement of active component properties, including such notable benchmarks as cell efficiency.

G. Novel Materials for Solar Power Applications

Considerable opportunities exist to adapt new high-performance materials derived from other technologies to systems for solar energy production and management. Particularly intriguing examples are offered by such items as protective coatings obtained by the plasma polymerization of network glasses (e.g., amorphous carbon) or the greatly enhanced barrier properties and toughness afforded by liquid crystalline polymers. The latter materials, representative of broader classes of high performance polymers, have significant potential to improve the performance of thin-film architectures, given the great flexibility of molecular synthesis. The cost impact of these material choices can be mediated by employing them as coherent, high-quality thin films (i.e., films of low mass coverage). The engineering associated with such applications is not broadly understood, especially with respect to chemically and topographically complex substrates, and will require the collaboration of interdisciplinary efforts to find solutions to problems of materials choice and manufacturability.

H. Mechanical Stability of Solar Multilayers

The use of multilayer structures for solar reflectors, PV devices, electrochromic windows, etc., implies the use of vapor-deposited thin films on dissimilar materials. Examples are silver deposited on polymethylmethacrylate (PMMA) for reflectors, and amorphous silicon/polycrystalline-metal interfaces in PV devices. One important consideration in the use of multilayer structures is the existence of stresses that can lead to damage or time-varying performance [12]. The stresses can be residual stresses originating from the fabrication process or stresses arising as a result of thermal excursions during service. Depending on the nature of the interface, residual stresses may arise from coherency or from the service temperatures being different from the fabrication temperatures. Finite-element-method (FEM) analysis of adherent thin films subjected to thermal excursions reveals that significant in-plane shear and axial (perpendicular to the bonding plane) stress may develop as a consequence of different coefficients of thermal expansion.

The residual stresses may cause time-dependent plasticity failures at ambient as well as at elevated temperatures. This mode of failure may occur by (although it is not restricted to) time-dependent plasticity leading to cavitation and ductile microvoid coalescence. Residual stresses can also lead to environmentally induced fracture such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), or metal-induced-embrittlement (MIE). An additional mechanical complication may occur with repeated thermal excursions during service of the multilayer (consisting of both active and passive components). The differences in thermal expansion coefficients of the components will lead to alternating mechanical stresses. These alternating stresses can lead to the failure processes described above for "monotonic" loading. More insidiously, the cyclic loading may lead to plastic deformation within the interlayers or interfaces that leads to lower stress fatigue-type failures.

The vulnerability of multilayers to these failure mechanisms can, of course, be determined experimentally, a process that may require lengthy and extensive testing to verify reliability for a variety of candidate multilayers, environments, thermal histories, and processing conditions. A useful complement to a purely experimental approach is comprehensive stress analysis. Residual stress analyses (perhaps using X-ray measurements) together with a prediction of the variation of the thermal stresses with temperature permit an estimate of the stress state evolution during service. Estimates of the vulnerability to environmentally induced and brittle fracture are possible. Naturally, plasticity relaxes the stress and can lead to other damage. Constitutive relationships for multilayer components could predict the stress relaxation and plastic strain levels, thus providing insight into the potential vulnerability to failure by monotonic and cyclic loading.

We emphasize that because the interfaces are vulnerable to failure, some form of modification of the interfaces may lead to longer lifetimes. Strategies for enhancing durability while maintaining performance should be examined.

1. In Situ Diagnostics for Manufacturing Processes

The impact of surface processing on the materials used in technologies for energy production and conservation needs to be monitored in situ in a nondestructive way to provide process control. The important criteria for adhesion, electrical properties, and nucleation and growth of adlayers are the morphology or structure and composition of the surface. Another critical area in multilayer devices is the role of the individual component films (structure-function relationships) in determining the overall mechanical integrity of the device.

The structures of concern here are generally layers deposited and modified in vacuum by ion beam and/or plasma techniques (this volume, Chapters 12, 13, 15, and 16). The process control parameters to be considered include surface preparation, temperature, bias voltage, plasma composition, residual gas composition and base pressure, and deposition pressure and rate. (Implicitly included is reactor design.) Through manipulation of these parameters, the surface and thin-film properties can be adjusted in a controlled way to yield complex structures with specifically designed properties. Thin films of polymers are also likely to be of considerable interest, and the analysis of coating and bonding processes will present different but equally demanding challenges.

Research opportunities exist in two areas. The first of these is the development of manufacturing diagnostics based on surface and plasma analysis techniques that operate both in real time and in situ. The characteristics of the probes will depend very strongly and sensitively on the class of material or deposition process being monitored. In the second area of research, the techniques developed above must be integrated into automated process controls for manufacturing. Specific directions and evaluations of trends for automated process control are given in Chapter 26 of this volume.

J. Accelerated Life Testing (ALT)

Accelerated life testing is essential for exposing weaknesses in thin-film multilayer solar collectors. It serves a number of functions such as securing a relative ranking of several competitive designs or the comparative stability of the same design and fabrication by different manufacturers. Mechanistic work at a molecular level is an essential complement to ALT. The needs and opportunities in ALT and how they relate to this chapter are given in Chapter 25, this volume.

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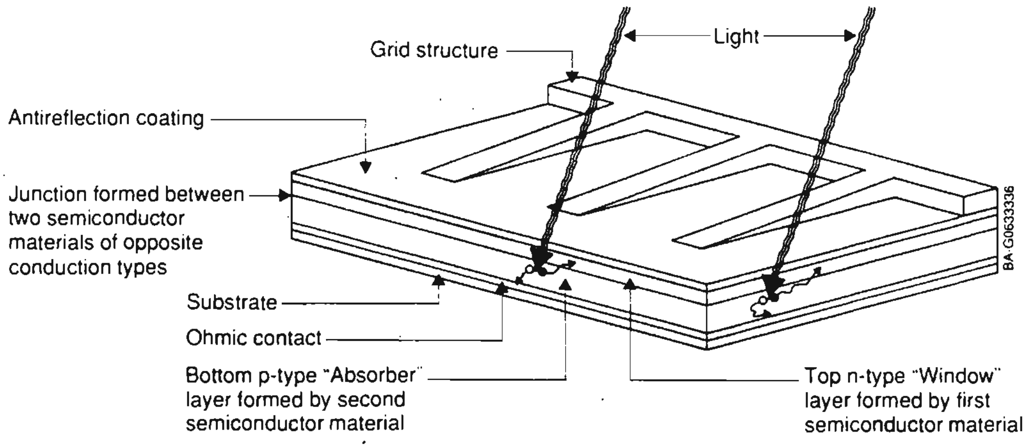


Figure 1. Typical photovoltaic solar cell

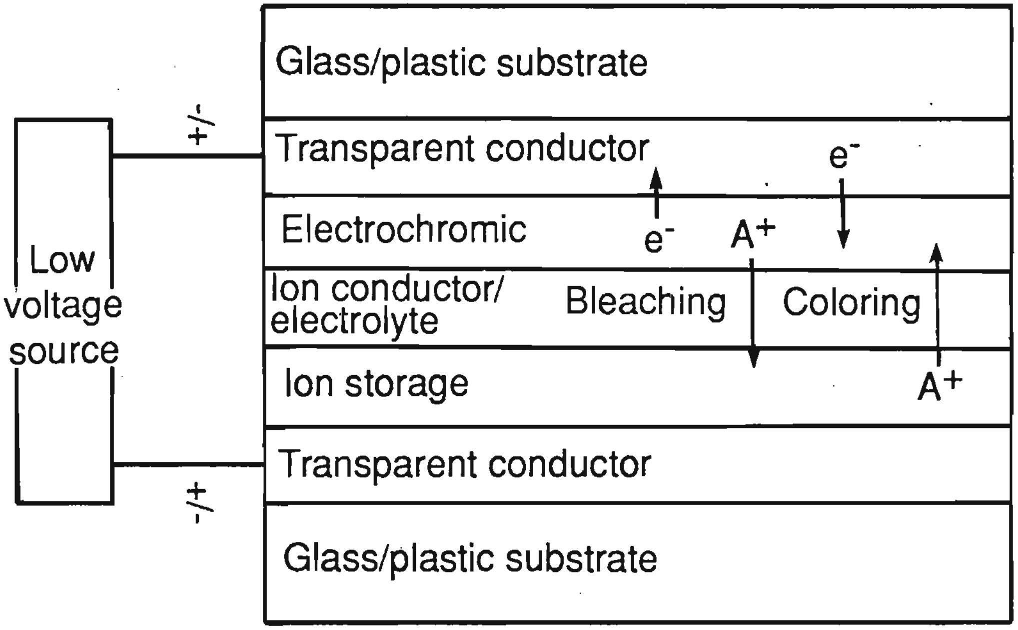
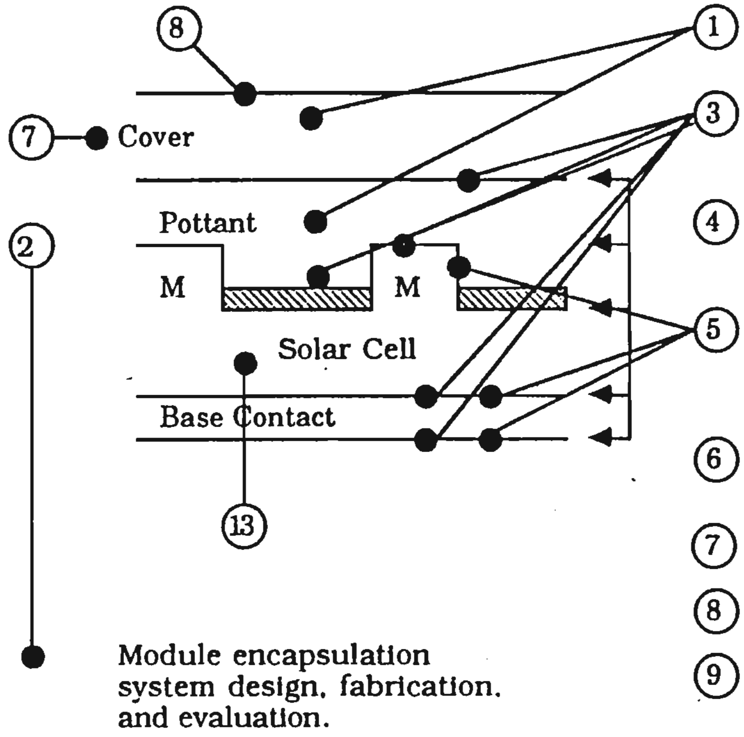


Figure 2. Schematic of an electrochromic window



MODULE DESIGN AND DEGRADATIVE REACTIONS/PROCESSES

① Photo-thermal degradation of polymers (pottants, covers, screens, adhesives)

③ Catalyzed degradation polymers/M or oxides; interdiffusion.

④ Permeation of H_2O, O_2, other gases, into the module.

⑤ Electrochemical corrosion, corrosion, $\vec{E}$ induced or e-injected pottant degradation, delamination of M or other components.

⑥ Accelerated aging and lifetime prediction.

⑦ Cover plate modification

⑧ Soiling of cover plate

⑨ Electrical isolation of cell string and other module components.

⑩ Module prototype development

Figure 3. Cross-section of a solar cell in an encapsulated PV module and some key durability issues

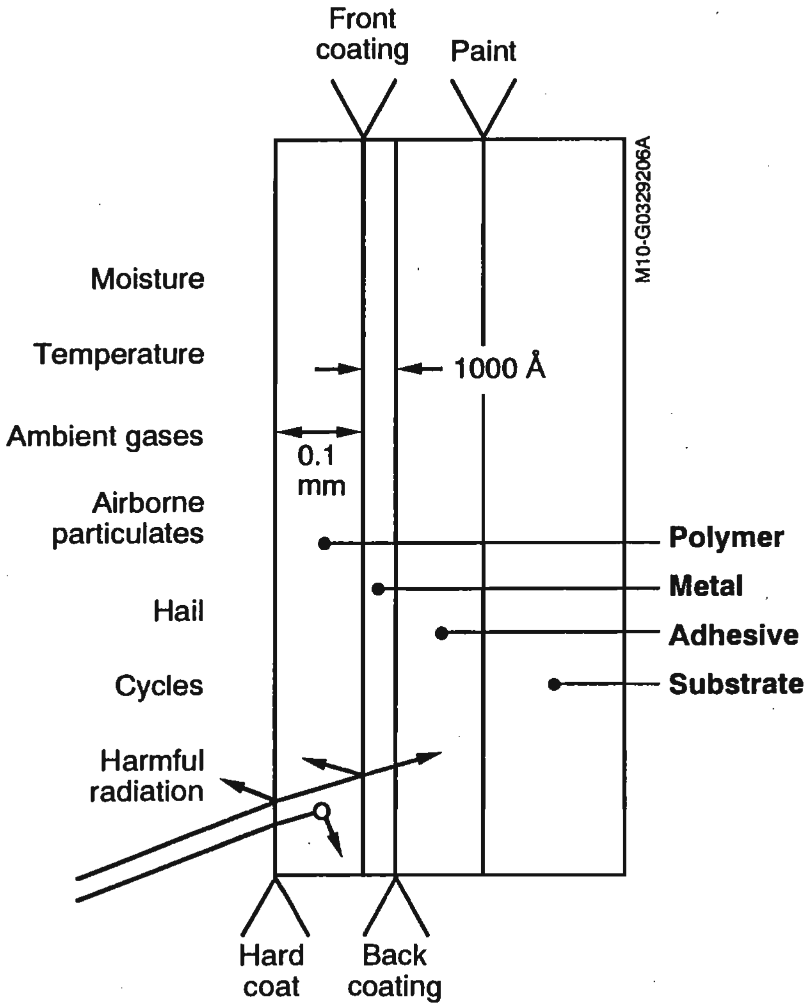


Figure 4. Schematic of a silvered polymer mirror

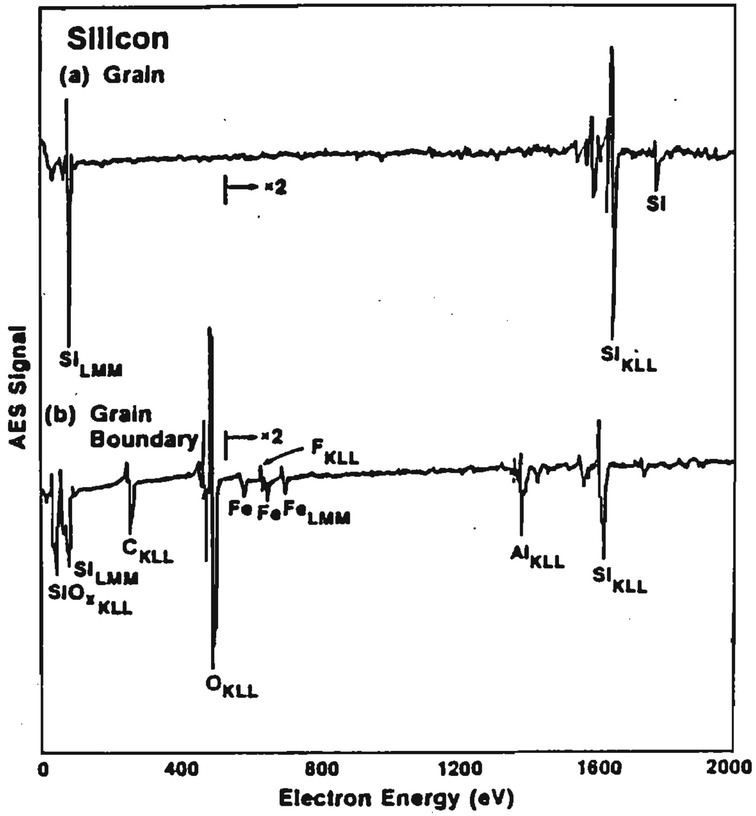


Figure 5. Impurities at grain boundaries in silicon used for PV cells

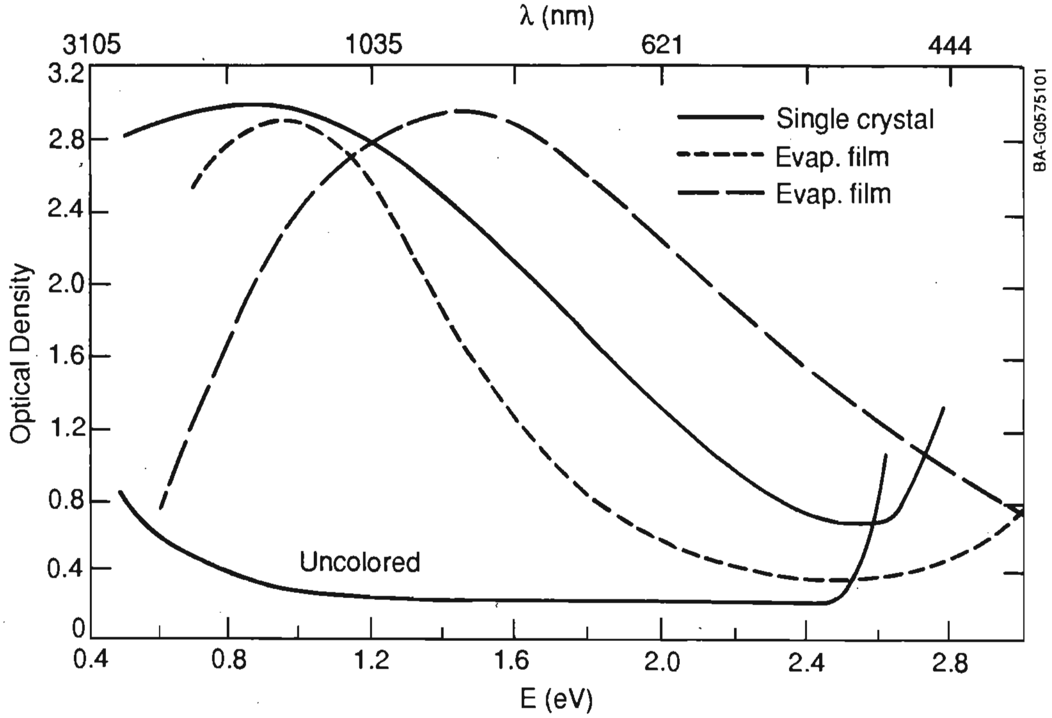


Figure 6. The transmittance of an electrochromic window in the bleached and darkened states

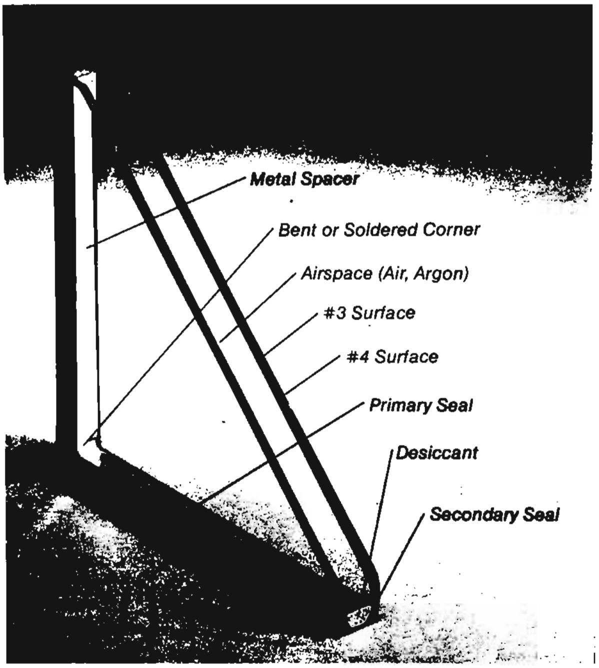
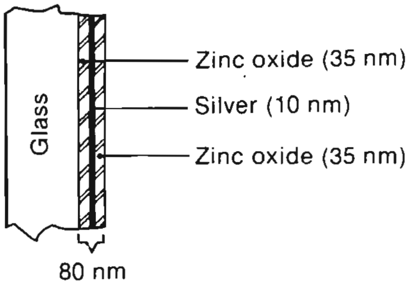
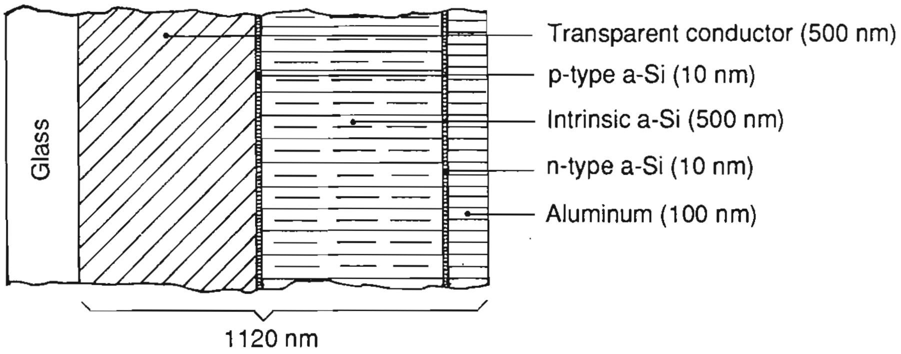


Figure 7. Contemporary two-pane glass window in which a Lo E coating is deposited on the #2 surface. In future energy-saving windows, the coating may consist of semitransparent PV materials and/or an electrochromic device.

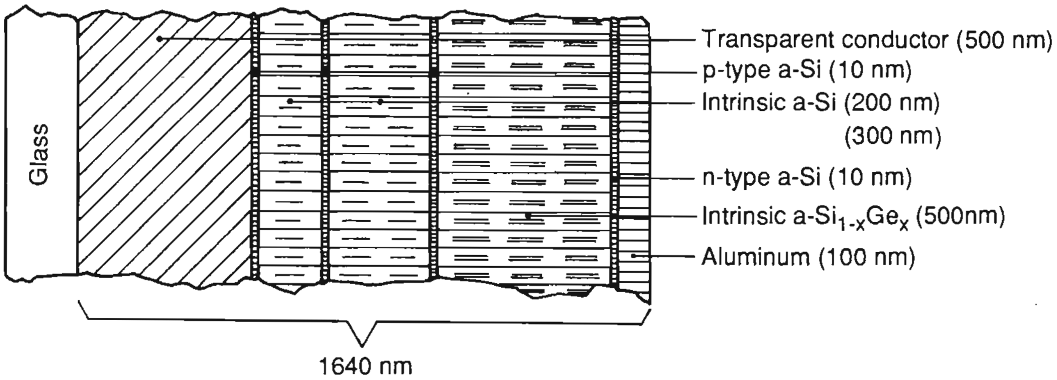
Low-e Coating



Thin Film a-Si PV Cell



Thin Film, Two-Terminal, Multijunction PV Cell



Electrochromic Coating

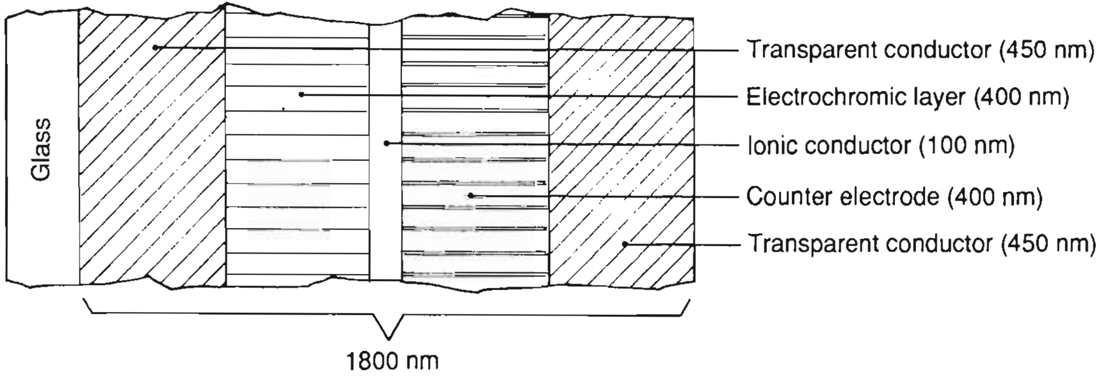


Figure 8. Relative thicknesses and typical components in Lo E glass, a-Si:H PV, and thin-film PV multilayers, and an electrochromic window

25. ACCELERATED LIFE TESTING OF DEVICES WITH S/S, S/L, AND S/G INTERFACES

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I. INTRODUCTION

The mission of the task group on accelerated life testing was to "Identify those areas in a service life predicting methodology used in a natural weathering environment that require additional resources." The efforts of this task group support the overall goals of the other Task Groups in the Surface Processing Workshop.

The "natural weathering environment" includes the primary weathering stresses of light, heat, and water plus the effects of airborne particulates (dust and dirt), pollutants, acid rain/dew, and biological agents (mildew, algae, etc). No particular device or material was emphasized in these discussions, but rather an overall evaluation of the current state of service life predictions for materials, in general, was considered.

Because emerging advanced materials demonstrate ever increasing lifetimes, new approaches to service life prediction are necessary. For example, significant improvements in the lifetimes of polymeric materials—up to 10, 20, or 30 years—are anticipated.

The use of "natural" weathering at exterior exposure sites to establish service life is no longer viable for these long-lived materials. Recent generation automotive coatings have exhibited substantial gloss loss and, sometimes, color shift in 1 to 2 years of Florida exposure. With the advent of "base coat/clear coat" technologies, automotive coatings now show little change in 5 to 10 years of similar exposure. The introduction of fluorocarbon paint systems may well increase lifetimes to 20 to 30 years as they have in architectural coatings. To have a reasonable economic payback compared with current energy alternatives, solar energy devices will require lifetimes of 20 to 30 years plus.

Obviously, this means that accelerated test methods will become even more important in the near future than they have been in the past. Unfortunately, many material scientists have been disillusioned in their attempts to predict material performance in exterior environments from the results obtained from accelerated aging tests.

The first part of this chapter will discuss the reasons for some of the frustration of lifetime prediction and, therefore, the need for new approaches to service life predictions. These new methodologies will require significant resources and a multidisciplined approach to address this complex and very difficult problem. These new approaches and information gaps will be described and research areas will be identified that will be needed to make these new methodologies workable.

II. SERVICE LIFE METHODOLOGIES

A. Linear Model

This method has been and is still being used to "correlate" accelerated tests to natural exposure environments. The typical approach is to test a material both outdoors and in an accelerated test. Assuming similar failure modes, the time to reach a predetermined property change is determined for both tests. These two times are related through a linear (zero intercept) equation.

$$k_a t_{accel} = t_{actual}$$

where: t_{accel} = time in accelerated test
t_{actual} = time in exterior or field environment
k_a = constant

Rearranging this equation gives the more common form in which k_a is often referred to as an acceleration factor.

$$k_a = \frac{t_{actual}}{t_{accel}}$$

Many of the accelerated weathering specifications that control commerce for both industry and government are established using this approach. Unfortunately, most of the time, these acceleration factors are determined from experiments using only one material and a single point exposure in each environment. Typically, there is no replication for the accelerated test or outdoor exposure. This means the k_a factor is often fraught with undefined sample, property measurement, exposure test, climatic, and seasonal variations. Once a k_a has been established for a material, it is often erroneously extrapolated to other materials that inherently have a significantly different acceleration response in the same accelerated test.

Simms [1] has described the problems associated with linear correlation models and has proposed a methodology for determining valid "accelerated shift factors." Many sample replicates (both accelerated and real environments) are required for these calculations, and each material will require the calculation of the material-dependent k_a. Even the calculation of a statistically valid k_a does not really define the performance of the same material during a re-exposure because of the high variability of both accelerated and outdoor exposures [2,3]. In any single test, premature or delayed failure may be the product of test variability and not true material performance. In addition, using an approach that requires the exposure of a material to both accelerated and real service environments, in order to establish test validity, is of questionable usefulness because the length of the experiment is always controlled by the duration of the outdoor experiment.

B. Nonparametric Statistics

During the early 1980s, the use of nonparametric statistics to relate accelerated to real weathering tests started to grow in popularity. The impetus for this methodology was originally attributed to the high variability of exterior exposure results (year-to-year climatic differences at a single site).

The nonparametric approach does not assign an absolute level of performance (or failure) to a single material, but ranks the performance of a series of materials. In correlating accelerated and real exposure tests, the rank performance of a series of materials exposed to both environments is compared, and the strength of the association between the tests is established. This is shown in Table 1.

Table 1. Example of Rank Performance

Material	Rank in Accelerated Test	Rank in Exterior Exposure
A	1	1
B	2	2
C	3	3
D	4	4
E	5	5
F	6	6

The ranks can be determined from actual material property measurements such as physical or chemical properties, subjective observations, or time to a defined property change or failure. The above example would be the ideal case of perfect correlation. Several measures of nonparametric correlation have been described by Conover [4]. Spearman rank correlation coefficients (r_s) are most commonly used for relating weathering tests.

$$r_s = 1 - \frac{6\sum d_i^2}{n(n^2-1)}$$

where d_i is the difference in the ranks for each material in each test and n is the number of materials tested.

Values for r_s range from 1, indicating perfect agreement between the accelerated aging and outdoor exposure rankings, to -1, indicating a perfect reverse ranking. A correlation coefficient of zero indicates that the accelerated and outdoor exposure rankings were random or showed no agreement.

Spearman's r_s is a measure of the tendency for "reversals" between the two tests. Ranking sample performance ignores the effect of test variability caused by differing primary stress levels. Round-robin studies indicate that nominally similar tests can cause significantly differing failure rates [5], but rank performance for a series of materials is quite reproducible between laboratories. In these cases, differing stress levels do not affect the failure ranking of materials, just the time required to achieve failure. Ignoring the effect of stress level on failure rates means that actual service life predictions with associated confidence levels cannot be achieved. This is possibly the biggest weakness of the nonparametric approach. Service life of new materials can only be "ranked" relative to materials with known service lives, i.e., more or less—compared to the known material.

Another weakness of the nonparametric approach is in defining "What is good correlation?" Nonparametric methods were developed to evaluate, generally, low-level correlation between cause and effect. High levels of correlation (even 0.9 and above) can still allow significant, individual sample reversals to occur, especially in large sample sets.

Spearman rank correlation has most successfully been used in accelerated test development [6]. Accelerated test conditions are modified until rank correlation to exterior exposure is maximized. If high rank correlation accelerated tests can be developed for a broad range of material types, one may assume that this test has a "better chance" of properly ranking new materials.

Through the use of nonparametrics, unrealistic stresses, such as short-wavelength ultraviolet (UV) radiation not found in terrestrial sunlight or unrealistically high temperatures, have been eliminated. This has led to longer accelerated test periods—not the right direction to be heading for today's more durable materials. Accelerated test speed and high rank correlation are diametrically opposed. As the stresses in the accelerated test approach service conditions, the rank correlation coefficient will approach unity, but the test is no longer accelerated.

III. PRIORITIES FOR VALID SERVICE LIFE PREDICTIONS

The following sections will describe an idealized approach to service life predictions for highly durable materials and devices. The working group identified five priorities:

- Adopt a new service life prediction methodology for weathering environments
- Develop appropriate models for predicting "real" service life from accelerated tests
- Quantify the stresses in exterior environments
- Define and understand degradation mechanisms and their relationship to weathering stresses
- Establish data bases for quantified climatic stresses and material responses to these stresses.

The task group members are not naively presenting this proposal as being easily within reach. This is, by no means, a short-term or simple answer to the problems inherent in "weathering" service life predictions developed by current practices. Substantial resources and time will be required to predict effectively the service life of a new material or device with a high degree of confidence and, more importantly, with accuracy.

A. Service Life Models—Life Distribution Methods

A distribution of failures from worst to best is required to get a truly useable estimate of service life. Often when exposure tests are performed outdoors or indoors, single samples or, at best, duplicates or triplicates are tested, and an estimate of mean performance is obtained. In actual use, often the first few failures are the most important in satisfying consumer expectations or setting reasonable warranty periods.

Nelson describes several parametric statistical approaches that allow actual lifetime distributions to be established [7]. Confidence levels can also be determined for the distribution. All of these approaches require that many sample replicates be tested. This apparent disadvantage is offset by the fact that test times can be significantly shortened. Through "censored" data analysis techniques, only the first few failures have to be observed to get an estimate of the total service life distribution.

Two life distribution methods that seem most appropriate are the log normal distribution and the Weibull distribution. The log normal distribution is

$$F(t) = \Phi\{(\log(t)-\mu)/\sigma\}$$

where F(t) is the cumulative fraction failed, t is the time, Φ is the standard normal cumulative distribution function, μ is the scale parameter, and σ is the shape parameter.

and the Weibull distribution is

$$F(t) = 1 - \exp[-(t/\alpha)^{\beta}]$$

where F(t) is the fraction failed, t is the time, α is the scale parameter, and β is the shape parameter.

The strength of the proposed technique is that one should be able to predict the early times to failure and to establish a functional relationship between shape and scale parameters and the kinetics of degradation. This will facilitate the extrapolation and interpolation of these predictions to other service conditions. In addition, statistical discrimination among factors (material, processing, application, design, and environmental) may identify the factor or factors responsible for causing the unexpectedly short time to failure. Along with the early failures (infant mortality), normal wear out can also be modeled. Life distribution models can also handle multiple failure modes; this becomes more important when more complex systems or devices are tested. Martin and McKnight have demonstrated the utility of the Weibull distribution in rapidly describing the service life of various coating/metal substrate systems in corrosive environments [8].

Computer software packages are commercially available for these maximum likelihood methods, which can provide product life distribution estimates and confidence limits for specific test design stresses.

B. Models for Relating Real Life and Accelerated Tests

The most difficult challenge will be in the development of life-stress models that will "convert" accelerated test-life distributions to real life distributions. Single stress models have been successfully used on many occasions, most notably the Arrhenius relationship for relating failure rate to exposure temperature, i.e.,

$$\text{(failure) rate} = A\exp(-E/kT)$$

where E is the activation energy, A is the pre-exponential constant relating to test conditions and material characteristics, k is the ideal gas or Boltzmann's constant depending on equation units, and T is the temperature in degrees Kelvin.

In the more complex (multistress) world of weathering, an Arrhenius-type extrapolation was used to predict the failure of automotive interior materials exposed to various temperatures and solar radiation levels [9]. Most often, successful models in weathering will require accounting for a minimum of three stresses—light, temperature, and moisture.

The generalized Eyring model can be used to describe failure rates relative to temperature and one additional stress variable [7].

$$\text{Product lifetime} = (A/T)\exp(B/kT)\exp\{V[C + (D/kT)]\}$$

where V is the additional stress variable and A, B, C, and D are the constants estimated from the data.

Often, the additionally modeled stress has been humidity. Murray used a modified Eyring model to predict the service life distribution of magneto optics at various temperatures and humidities [10].

If a material or device being weathered is primarily sensitive to only two stresses, the Eyring model may indeed be adequate. Exposures in desert regions could use this model with "light" being the V stress while ignoring the effects of moisture. Carlsson suggests that for "electromagnetic stresses," the acceleration factor should be described as $(I/I_o)^P$, where I is the intensity of photoreactive light, I_o is a reference intensity, and P is a constant [11].

Most often, one would expect that models with three or more stress variables will have to be developed. Nelson describes generalized log-linear relationships for predicting multiple stress environments, but simple linear relationships will probably not be adequate [7]. Tobias and Trindade describe the addition of a third exponential multiplier to the Erying model equation to accommodate three stresses [12].

An added complexity arises because weathering involves nonconstant or cycling stress levels. This may require the development of a cumulative damage (exposure) model to relate the cyclic outdoor stresses to the "more constant" accelerated test.

Whatever form and complexity the modeling equations take, the stress levels, both outdoors and in accelerated tests, will have to be quantitatively characterized in a manner that facilitates comparisons between outdoor and accelerated exposure results.

C. Quantify Stresses in Exterior Weathering Environments

Proper accelerated weathering tests cannot be developed nor can real weathering environments be modeled without a thorough understanding and quantification of the stresses that cause material/device failure. Unfortunately, the United States is taking backward steps in gathering climatic data in a number of exterior environments.

Consistent methods of stress measurement, especially UV radiation, have not been established. The comparison of solar irradiance data from neighboring commercial, exterior exposure sites in both Florida and Arizona indicates that much work is needed in standardizing measurement techniques and calibration procedures for radiometers. Much better characterization of terrestrial solar UV, especially around 300 nm, will be needed for long-range lifetime predictions.

Temperature must be measured in a way that will quantify the thermal influence on both photoinitiation and subsequent thermally controlled reaction rates. Surface and internal temperatures, rather than ambient air temperature, of materials and devices would be more relevant to predicting failure rates. Determination of the efficiency of photodegradation as a function of temperature during exposure could lead to development of a UV radiation/thermal stress unit. Somewhat analogous to a heating degree day, this "thermal dose" might be helpful in establishing cumulative damage models for variable condition exterior exposures.

The various forms of water stress should be measured. The effects of dew and rain could be quantified by time of wetness (TOW) as is now done at a number of commercial sites that conduct exposure tests. Several TOW methods and devices are readily available. Relative, or more appropriately, absolute humidity (both during photo- and thermal-stress periods and dark periods) and total liquid precipitation can be easily quantified. It is also essential to understand the effects of moisture on surface and bulk degradation. In other words, we must know which form of water is most important—water vapor, condensation (dew), or rain.

Pollutants in several forms need to be characterized and quantified. Both dry deposited NO_x, SO_x, and acid rain or dew can have significant impact on material failure rates. Airborne particulates can either accelerate or retard photo-induced degradation. High altitude and terrestrial ozone levels impact solar spectral energy distributions and material oxidation rates, respectively.

The task group recommends that a coordinated, publicly funded program be developed through a single agency to monitor climatic stresses. Important aspects of this study might include:

- Three years of continuous stress measurement
- Six to 10 sites of various climatic classifications (desert, subtropical, high altitude, temperate, urban-polluted, marine)
- Identical, standardized, controlled, and calibrated stress measurements must be conducted at each site for the following:
  - Light: Total and spectral UV radiation at latitude angle
    Total global radiation at latitude angle
    Narrow band measurement at 310 nm
  - Temperature: White and black panel at latitude angle
    Ambient temperature
  - Water: Time of wetness
    Total liquid precipitation/frequency
    Humidity
  - Pollutants: NO_x, SO_x levels
    Total suspended particulates.

Continuous or long-term measurements of the specific climate factors listed above will allow for the development of models that can be used to estimate the stresses for many geographic locations based on more limited data collected at those sites. However, the efforts for precision characterization of climatic stresses should be combined with simultaneous exposures of a variety of materials at the same sites in order to model the effects of specific climatic stresses on polymer degradation. See Section E for more detail.

D. Defining and Understanding Material Degradation Mechanisms

This is probably the most critical area requiring extensive research before valid service life predictions can be made for a variety of materials. Once climatic stresses are defined, their impact on material failures must be fully understood. This will require characterization of materials before, during, and after exposure to weathering stresses. The task becomes even more complex when materials are combined to make components and devices.

It is not the intent nor necessarily the expertise of this task group to recommend specific characterization methods or analytical techniques that should receive special emphasis. Several applicable techniques are discussed in Chapter 26 on Interfacial Microchemical Characterization Needs in Surface Processing. An exhaustive review of analytical procedures particularly relating to coatings has been written by Anderson [13].

Surface characterization is extremely important for understanding the processes that occur at exposed surfaces and unexposed interfaces. Therefore, techniques that emphasize surfaces and interfacial boundaries will be especially useful.

Understanding the mechanisms and quantifying the kinetics of degradation reactions have several important benefits. If these processes are understood for materials in a natural weathering environment, the design of appropriate accelerated tests is made much easier. Accelerated tests can be modified until they produce degradation processes similar to those that occur in exterior weathering. The simulated stresses can be increased until maximum acceleration is achieved while still maintaining a service life failure distribution that can be modeled relative to an outdoor environment.

Ideally, if the basic failure processes are understood, and the defects or sites for failure are initiation are identified, the accelerated test may not be necessary. Service life could actually be predicted from results of material or product characterization by appropriate analytical techniques. Analogous to genetic code, all the information to predict service life is inherently contained in each individual specimen, if only it can be extracted and understood.

E. Climatic Stress and Material Response Data Bases

The climatic stress data that would be gathered from the general program described earlier should be maintained by a central, controlling agency. In conjunction with the climatic stress data collection, a broad selection of appropriate materials/systems should be exposed simultaneously at the same sites. Material response to these stresses should be measured and stored to aid in accelerated test design and ultimate service life projections.

Proper design of a comprehensive stress measurement and material response study is extremely critical. At the very least, the following points should be considered:

- Structure or composition of specimens
- Test conditions for sample mounting, exposure type, and exposure angle
- Initial material properties in which the measurement technique to characterize properties is a standardized procedure for making meaningful data comparisons between sites
- Material properties during and after exposure
- Corresponding cumulative stress levels at times of property measurement or material failure.

If properly planned and executed, the above weathering stress/material response data base could serve as the basic structure for an ever-growing national repository on weathering and materials. In general, most of the data on material response to weathering environments is held captive in the private sector, although some information specific to solar energy materials has been reported [14,15]. There is a need for a centralized data base on materials and weathering. A data base manager would be required to maintain and update information. The data base information could be segregated into material types or, possibly, end uses, such as protective coatings, optical materials, pottants, etc. Certainly, standardization of stress and property measurement would be extremely critical for this to be a useful source of information.

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26. INTERFACIAL MICROCHEMICAL CHARACTERIZATION NEEDS IN SURFACE PROCESSING

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ABSTRACT

Interfacial microchemical characterization is required for all aspects of surface processing as applied to transportation and utility technologies. Corrosion protection, fuel cells and batteries, wear surfaces, polymers and polymer-oxide interfaces, thin-film multilayers, photoelectrochemical systems, and organized molecular assemblies are a few examples of interest to these industries. A number of materials and processing problems, both related to fundamental understanding and to monitoring manufacturing operations, have been identified in which our microchemical characterization abilities are lacking. More than 20 areas for research are identified in which progress will contribute to improved understanding of materials and processes, improved problem-solving abilities, improved manufacturing consistency, and lower costs. Some of the highest priority areas for research include: (1) developing techniques and methods with improved chemical specificity at interfaces, (2) developing fast, real-time surface and interface methods, and (3) improving the cost and reliability of manufacturing monitors. Increased the collaboration among university, industry, and government laboratories will be required for progress to be made in a timely manner.

I. INTRODUCTION

Interfacial microchemical characterization plays a crucial role in both developing and improving surface processing of materials for the automotive and utility technologies. Within the automotive industry, there are a number of driving forces that demand that new materials and new kinds of material interfaces will be used. These driving forces include the need for reduced emissions, improved fuel economy (including lighter weight materials), improved safety, reliability, durability, and lower cost. Some specific automotive or utility interfaces might include a surface-modified engine cylinder bore; a composite body panel adhesively bonded to an automotive frame; the topcoat, primer, and conversion coating layers on a galvanized steel body panel; and multilayer films on a photovoltaic cell.

In this report, we have organized the issues involved in interfacial microchemical characterization needs as a 2 × 3 matrix, as shown in Fig. 1. On one axis, issues can be divided as pertaining either to fundamental and applied laboratory studies or to monitoring of manufacturing operations. Time-scale considerations are important here. Some studies to increase our fundamental understanding can take years. Other problem-solving studies (including failure analysis on field returns) may involve a couple of days. Characterization work related to material acceptance might take minutes or hours. Finally, in situ monitoring of a manufacturing line and accompanying process feedback take place on a time scale of seconds. We will discuss later the strong need to shorten all of the above time scales. In this report, we deal with improvements and extensions of existing techniques and methods. No attempt is made to be clairvoyant or to predict major breakthroughs. For example, the discovery of an inexpensive, easily processed, room-temperature superconducting material would rather dramatically change the course of both automotive and utility technologies.

The other axis in our organization matrix divides issues into three categories: (1) the motivating problems related to materials and processing, (2) the limitations of our current techniques and methods, and our needs to improve the situation, and (3) issues relating to information or infrastructure subjects, which go beyond the more narrowly focused subject of interfacial microchemical characterization. The issues, needs, and proposed areas of research we list in this report are meant to lead to near-term improvements in surface processing for automotive and utility applications. There is another workshop report that is still timely that discusses more basic research opportunities in interfacial microchemical characterization [1].

II. MATERIALS AND PROCESSING PROBLEMS

A. Fundamental and Applied Laboratory Studies

The variety of material interfaces that impact automotive technology is impressive. Interfaces can be solid-solid, solid-liquid, and solid-gas. Material types can be metals, oxides, inorganics, organics, polymers, and semiconductors. Some typical systems are given in Table 1, and the surface and interface tools we use to characterize these systems are given in Tables 2 and 3. Every material interface has a number of attributes that are critical to the performance of that interface, attributes such as chemical composition, chemical structure, defects, morphology, and roughness. These attributes in turn govern other material properties, such as corrosion resistance, hardness, diffusion, stability, and other interactions with the environment.

Significant interface problems involving materials and processing are listed in Table 4. One of the most important problems deals with so-called buried interfaces. These are solid-solid interfaces that are too deep for our wide variety of surface analytical tools to probe without resorting to intricate specimen preparation or model systems. We need to know a good deal about these solid interfaces (see the list above regarding composition, structure, defects, etc.). We also need to characterize these interfaces on a variety of spatial scales, ranging from a mm scale to a μm scale and even sometimes a nm scale. Ideally, we would like to have a nondestructive characterization tool to allow the interface to be examined following (or during) successive processing treatments or environmental exposures.

A second class of important interface problems deal with impurities, defects, and diffusion at interfaces. Impurities and defects are important because these features usually initiate interfacial failures. The investigator needs to determine the identity of an impurity (or defect), to determine how much is present, and to determine the spatial distribution. For studies of diffusion and interdiffusion, the investigator determines the type of diffusing species, the rates of diffusion, and the effect of the diffusion on the interface. Representative automotive technology examples are (1) the diffusion of methanol-hydrocarbon fuel mixtures at surface-treated polymeric fuel tanks, (2) the diffusion and intermetallic compound formation at layer interfaces of journal engine bearings, and (3) interdiffusion across metal-semiconductor interfaces of integrated circuit sensors subjected to the elevated temperatures of the underhood environment.

Another interfacial problem is nonideal surface (and interface) topography. Manufactured surfaces have roughnesses that make the application of our conventional surface science tools difficult or

Table 1. Typical Material Interface Systems in Automotive and Utility Technologies

Solid-solid	Metal-metal	– galvanized steel – brazed aluminum radiators
	Metal-oxide	– electrically heated windshield
	Metal-inorganic	– phosphate conversion coating on steel – chromate coating on aluminum – Pt electrode on zirconia exhaust gas oxygen sensor
	Metal (oxide)-organic	– adhesive on surface-modified metal
	Metal-semiconductor	– ohmic contact on an integrated circuit (IC) device
	Semiconductor-semiconductor	– diode (e.g., GaAs on Si)
	Polymer-polymer	– paint system on thermoplastic part – adhesive on sheet molding compound
	Fiber-matrix	– carbon fiber-reinforced epoxy
Solid-liquid	Metal-electrolyte	– lead-acid electrochemical cell
	Polymer-organic	– surface-treated polymeric fuel tank
Solid-gas	Oxide-gas	– SnO_2-type combustion gas sensor

Table 2. Listing of Techniques for Microcharacterization of Solid Surfaces and Solid Interfaces

Inherently Surface Sensitive	XPS	X-ray photoelectron spectroscopy
	UPS	ultraviolet photoelectron spectroscopy
	AES	Auger electron spectroscopy
	SIMS	secondary ion mass spectrometry, including ion microprobe (IMP), time-of-flight (TOF), secondary neutral mass spectrometry (SNMS), and other post-ionization methods
	STM/AFM	scanning tunneling microscopy, atomic force microscopy, and other proximal probe microscopies
	LEEM	low energy electron microscopy
	ISS	ion scattering spectrometry
	LEED/RHEED	low energy (and reflected high energy) electron diffraction
	SEXAFS	surface extended X-ray absorption fine structure
	HREELS	high-resolution electron energy loss spectroscopy
	TDS	thermal desorption spectroscopy
	FIM/FEM	field ion/emission microscopy
	FE	fracto-emission
	WM	wetting methods
Less Surface Sensitive	SEM/ESEM	scanning electron microscopy, environmental SEM
	TEM/AEM	transmission electron microscopy, analytical EM
	RBS	Rutherford backscattering spectrometry, and other energetic ion methods: nuclear reaction analysis (NRA), proton-induced X-ray emission (PIXE), heavy ion backscattering (HIBS)
	EPMA	electron probe microanalysis
	TR-XRF	total reflectance X-ray fluorescence spectroscopy
	SAW	surface acoustic wave
Bulk Methods	IR	infrared spectroscopy
	Raman	Raman spectroscopy
	SE	ellipsometry, spectroscopic ellipsometry
	SHG/SFG	second harmonic generation, sum frequency generation
	EXAFS	extended X-ray absorption fine structure
	XRF	X-ray fluorescence spectroscopy
	XRD	X-ray diffraction, also neutron diffraction
	ESR	electron spin resonance spectroscopy
	LAMMA	laser microprobe mass analysis
	SPAS, PET	slow position annihilation spectroscopy, positron emission tomography

Table 3. Techniques for the Solid-Liquid Interface

– Optical (photon) methods, including nonlinear (laser) spectroscopies, light scattering, X-ray scattering, absorption spectroscopy	
– Various proximal probe microscopies	STM/AFM
– Spectroscopic ellipsometry	
– Attenuated total reflectance infrared spectroscopy, also reflectance IR, Raman	ATR-IR
– (X-ray with glancing angle techniques)	XRF, XRD
– (By "backside" RBS technique)	RBS
– Electrochemical potentiometry	
– Zeta-potential	
– Contact angle, air-bubble contact angle	
– Surface acoustic wave	SAW
– Total reflection EXAFS	TR-EXAFS

Table 4. Major Interfacial Characterization Problems Related to Materials and Processing

Fundamental and Applied Laboratory Studies	Monitoring Manufacturing
"Buried" interfaces	"Buried" interfaces
Defects, impurities, and interdiffusion at interfaces	Impurities at interfaces
Surface topography	Rapid real-time measurements
Stability, degradation, properties, and morphological phase of interfaces and thin films	Surface contamination

impossible. A final interfacial problem deals with numerous issues involving thin films, including stability, degradation, properties, and the morphological phase. The rates of chemical change need to be measured as well as the effect of a chemical change on the properties of the material or device. Often an in situ or nondestructive technique is required, but frequently no suitable technique is available.

B. Monitoring Manufacturing Processes

The most significant materials and processing problems involving manufacturing operations are listed in Table 4. Many of the same problems that appeared on the Laboratory Studies list also appear on the Manufacturing list. Furthermore, in the manufacturing environment, we have additional constraints concerning the time scale within which the measurement must be made and the requirement that the measuring probe must be nondestructive and nonperturbing.

Dealing with buried interfaces again makes the list of important needs. Currently, there are many instances in which information is required on the chemistry, morphology, or structure of a buried interface, but no monitor exists to provide the information. Obviously, development of new techniques and sensors to meet our monitoring requirements will be ranked as a high priority later in this report. A related matter, in-service testing monitors, would likewise benefit from any developments in new interface monitoring sensors. An in-service testing example involving utility technology is the testing of photovoltaic devices in a working array.

Other needs on our list include monitoring impurities at interfaces and surface contaminants. Again, frequently no suitable manufacturing monitor exists. The requirements here are (1) the detection of an impurity or contaminant, (2) its quantification, and sometimes (3) the characterization of an unknown impurity or contaminant. An example involving steps (1) and (2) is surface carbon contamination on steel, in which carbonaceous deposits interfere with the phosphate conversion coating operation. Finally, the high line speeds of many manufacturing operations pose a real challenge to developing suitable interface monitors that are capable of operating in "real" (that is, rapid) real time. For instance, an electrogalvanizing line for coiled steel operates at tens of meters per minute.

III. CURRENT LIMITATIONS AND NEEDS

A. Fundamental and Applied Laboratory Studies

A list of interfacial characterization needs is given in Table 5. We rank our needs into three categories: crucial, important, and useful. The first crucial need is for techniques and methods with improved chemical specificity at surfaces and interfaces. Chemical specificity includes chemical bonding information, sensitivity to hydrogen, and characterization of organics and macromolecules (includes conformation, isomerization, and cross-linking). A number of current techniques in common use are capable of chemical specificity (X-ray photoelectron spectroscopy [XPS] core and valence, secondary ion mass spectrometry [SIMS]/secondary neutral mass spectrometry [SNMS], high resolution electron energy loss spectroscopy [HREELS], infrared [IR]/Raman, sum frequency generation [SFG], thin-film X-ray diffraction [XRD], extended X-ray fine structure spectroscopy [EXAFS]/surface extended X-ray fine structure spectroscopy [SEXAFS], temperature programmed desorption [TPD]). These techniques also have the potential to detect hydrogen (except core XPS) and to characterize organics. However, a number of restrictions exist: the potential of the technique depends on (1) the problem addressed, (2) whether the specimen is a single phase or a mixture, (3) whether the specimen is stable under the particular probing beam of the technique, (4) whether the specimen is stable in the analyzing environment of the technique (vacuum environments may lead to loss of waters of hydration, decompositions of hydroxides, alterations

Table 5. Current Limitations and Needs in Interfacial Microchemical Characterization

Fundamental and Applied Laboratory Studies	Monitoring Manufacturing
Crucial:	Crucial:
– Chemical specificity (including bonding, hydrogen, organics)	– New, nondestructive techniques
– Real-time techniques for dynamic measurements in process environments	– Improved cost and reliability of monitoring methods
– New technique development	
Important:	Important:
– Specimen preparation	– To extract information
– Nondestructive methods	– Reference materials
– 3-D characterization	– Improved optical methods, coupled with optical fibers
– Extract maximum information	
– Reference materials	Useful:
– Model systems	– "Monolayer" detection on-line

of crystalline/amorphous morphologies), and (5) the requirement for unambiguous identification among closely similar species or contaminants. As a consequence of these restrictions on our current methods, any improvements in our ability to provide chemical specificity for material interfaces will be very beneficial.

The next need, which we ranked as crucial, was for the development of fast, real-time techniques for dynamic measurements in a process (in-situ) environment. Frequently, we need to monitor rapidly changing surface and interface features during a processing reaction (or for a model system of a technical process). Examples include diffusion, corrosion, film growth, wear, and catalysis. Some current techniques employed for real-time, in-situ work include SFG (µs time scale), environmental transmission electron microscopy (TEM)/scanning electron microscopy (SEM) (< 1 ms time scales), scanning tunneling microscopy (STM)/atomic force microscopy (AFM) (< 1 ms), ellipsometry (20 ms), IR (500 ms), and other, slower methods. Many other techniques might be appropriately engineered for rapid, in situ measurements, but the expense is very high. One "hybrid" instrument that may be useful for this topic is a combined environmental-SEM/environmental-AFM. Another proposed hybrid instrument is a combined SEXAFS/X-ray standing wave instrument.

The third crucial need is for the accelerated development of some recent new techniques. Included here are AFM, STM, near-field imaging, X-ray optical methods, and fiber-optic-based light microscopy.

There are six other needs that we rank as important. The first is for improved specimen preparation methods and reduction of experimental artifacts. Novel specimen preparation or experimental setup may enable us to substitute a classic "ex situ" method for a sophisticated, expensive "in situ" method with no loss of information. When multiple techniques or sequential techniques are used, the location of the analyzed region must be correctly identified. Beam damage and temperature effects must be minimized, or we risk invalidating the study. Refinements in preparation of cross-section specimens for TEM will extend this critical tool to more material interfaces to characterize defects, topography, and interfacial phases. Some current specimen preparation (or experimental setup) methods used to examine solid-solid interfaces with surface science tools include ion sputter-etching, mechanical sectioning (ball craters, radial sections), and in situ fracture. Some non-destructive experiments are also used, where the "take-off" angle is varied or the beam energy is varied. Improved methods would be welcomed.

The next important need is for improved nondestructive evaluation methods. As mentioned earlier, the need is to characterize a specific material surface or interface before and after a processing step, in order to determine the effect of the processing. Some of the light-based optical methods mentioned elsewhere in this report appear promising here. The relatively new positron annihilation techniques, such as slow positron annihilation spectroscopy (SPAS) and positron emission tomography (PET) are also worth mentioning. A third need is for improved three-dimensional (3-D) characterization, with high spatial resolution and chemical bonding information. Some leading tools that will undergo further improvement include 3-D SIMS mapping, 3-D XPS and Auger profile/mapping, X-ray tomography, analytical electron microscopy (AEM), and confocal light microscopy. One of the challenges with the data-rich 3-D techniques is dealing with data collection, analysis, and display. This is discussed later in our report. The fourth need is to use tools to extract maximum information from the experimental data. Often only a small fraction of the information that the analyst has expensively acquired is used, with the remainder discarded. Multivariate analysis methods are well established for improved data processing, but are not as widely used as they ought to be. Perhaps an expert system approach is required here. Included in this fourth need is the improvement of existing methods for quantification, specification, artifact removal, and the need to improve detection limits. Progress here will require improved measurements of some important physical parameters and improved knowledge of physical phenomena. The fifth need is for improved reference materials. Because we are dealing with material surfaces and interfaces, there are significant preparative challenges here, but we will improve our ability to calibrate our instruments and identify and characterize complex material systems. The sixth and final need is the development of better model systems. An appropriate model system is far easier to deal with in understanding a particular surface-processing phenomenon than dealing with the actual, more complex system; such model systems nevertheless have to be validated.

B. Monitoring Manufacturing Operations

Because of the additional constraints imposed on monitors in a manufacturing operation (simple, reliable, nonperturbing, low cost, rapid, etc.), the task of doing interfacial characterization in the manufacturing environment seems more difficult than in the laboratory environment. One saving factor, compared with laboratory studies, is that usually only specific information for a single parameter of an interface is required, not a full characterization. There are a limited number of monitors currently in use for dealing with surface processing and material interfaces. They include thickness measurements (by numerous techniques), mass spectrometry, X-ray fluorescence, thermography, glossimetry, radiography, ambient photoemission probe, and IR. Additionally, there are many monitors that perform measurements in an "off-line" mode to support manufacturing. Frequently the lack of a suitable monitor means that no measurement is done, and the control of the processing step is uncertain. Thus, we list the need for new, nondestructive techniques for rapid monitoring during manufacturing as a crucial need.

The other need listed as crucial is for improved cost and reliability of monitoring methods. Most of our surface science tools are too expensive and otherwise inappropriate for a manufacturing environment. Other measurement concepts from chemistry, physics, remote sensing, and nondestructive testing disciplines should be looked at as potential sources for improved monitors. Since the cost of computing hardware continues to decline, we will be able to process a great deal of information inexpensively. Methods with improved cost and reliability are likely to be computationally intensive, but to utilize simple probes, analyzers, or detectors.

We have ranked three other manufacturing needs as important. The first two, the need to extract maximum information from a measurement and the need for improved reference materials, also appeared on our laboratory studies list. Benefits to the manufacturing operations will include more accurate and more robust measurements. The third important area for development is in improved, light-based optical methods, coupled with optical fibers. This technology is especially suited to the constraints of a manufacturing monitor (low cost, high speed, ruggedness, flexibility, small size).

A final manufacturing need that would be useful is monolayer detection on-line. Some critical operations have a requirement for high sensitivity on a rapid basis. Our common schemes that have monolayer sensitivity (electron spectroscopy, SIMS, and others in Table 5) are usually unsuitable for a process environment. New approaches should be investigated.

IV. INFORMATION AND INFRASTRUCTURE ISSUES

A. Fundamental and Applied Laboratory Studies

A number of the needs that our group identified while looking at interfacial microchemical characterization needs for surface processing cannot be defined as projects for an investigator to develop, so they did not appear on the lists in the previous section. Instead, they are needs that must be more globally addressed by all investigators and their institutions for progress to be made. These issues, which appear in Table 6, are again ranked as crucial, important, and useful.

Table 6. Information and Infrastructure Issues

Fundamental and Applied Laboratory Studies	Monitoring Manufacturing
Crucial:	Crucial:
– Collaboration of University, Industry, and Government	– Collaboration of University, Industry, and Government
– Availability, sharing, and effective use of equipment and instrumentation	– Compressed time scale for method development
– Availability, sharing, and effective use of expertise and knowledge	
Important:	Important:
– Compressed time scale for studies	– Expert system development
– Greater use of existing knowledge	
– Availability and sharing of data	
Useful:	
– Techniques for data visualization	

The first crucial need is for increased collaboration among university, industrial, and government and federally funded laboratories. As our requirements become more complex, or interdisciplinary, or systems-oriented, more teamwork is required to develop an improved method or technique. Our imposed and our unconscious barriers that limit interactions among investigators will slow the development of solutions to the problems we are facing. There is also a prevalent "single investigator" frame-of-mind in many instances that hampers a team approach. The benefits from further collaboration include the generation of new ideas and approaches, more effective and efficient utilization of experts in different laboratories, and potentially shorter times for task completion.

The next crucial need, which is partially a subset of our increased collaboration discussion, concerns the availability, sharing, and effective use of equipment and instrumentation among the institutions listed earlier. Many surface and interface science tools are expensive. Further, many problems require information contributed by a variety of instruments to be successfully resolved. We recommend increased sharing of instruments and instrument time on a variety of levels, from lengthier joint research projects to quick problem-solving exercises. Compensation between institutions should be flexible, ranging from joint project agreements, to per-diem cost reimbursement, to informal reciprocal instrument-time agreements and mutual assistance.

The final crucial need, also partially a subset of increased collaboration, is to increase the availability, sharing, and effective use of expertise and knowledge. A list of action strategies, which is far from all-inclusive, includes (1) exciting student interest in interdisciplinary activities by exposing students to industrial problems, (2) regular exchanges among faculty, industrial scientists, and government scientists through sabbaticals, summer programs, and short visits, and (3) more involvement in planning at all institutions by scientists from all three groups.

We ranked three more issues as important. First, we need to compress the time scale of our studies. We spend too much time to complete our fundamental and applied studies, and future applications are delayed. Second, we must make greater use of existing knowledge. In the case of numerous applied studies and problem-solving exercises, time and effort is expended for unnecessary laboratory characterization work when the necessary information is already available from the published literature, colleagues, consultants, or other resources. In other cases, a useful technique may not be applied to a problem because its utility is not widely understood. For instance, valence band data are rarely acquired in XPS studies, even though considerable bonding information can be discovered using it. More training in using the existing methods of valence band interpretation is needed. Third, we should increase the availability and sharing of data (including material property and performance data, as well as chemical and analytical data). A wide range of data needs to be shared, not only to aid in the analysis of a specific problem, but to provide generally available data that may prove of value to other groups, including theoreticians and modelers. Institutions should work to minimize the requirements for proprietary data. Additionally, our research communities should agree on electronic formats for the easy exchange of information and data, and should encourage the formation and growth of national and international data bases.

A final, useful need is for more use of techniques for data visualization. Certain techniques, especially 3-D techniques like 3-D SIMS profiling/mapping, generate huge amounts of data. There are now some newer data visualization software packages that work well on engineering work stations and these packages will satisfy this need when their usage is more widespread. Additionally, some standard presentation formats may have to be agreed on. For instance, the images produced by STM and AFM experiments can be misleading when the data are massaged to simulate a photograph produced by light microscopy or electron microscopy. Thorough explanations of the data processing steps, and perhaps a sequence of intermediate processing images, may be required to adequately explain the information in an image.

B. Monitoring Manufacturing

For the manufacturing side of interface characterization issues, we again list a crucial need for collaboration of university, industry, and government and federally funded laboratories. For many years, there has been an inadvertent cultural barrier separating projects in pure science from manufacturing-related projects. As greater attention is focused on manufacturing-related projects from different sources, fresh approaches will result. The second crucial need is to compress the time scale for method development. If a process monitor takes months to set up, it probably won't be done. There is a cost associated with the delay in process monitor development. Another time scale associated with process monitors is the time between the data acquisition and the processed result. No process action can be taken until the information is fully processed, so data processing and response time should also be as short as possible.

A final, important need for monitoring manufacturing is for more expert system development. This approach is useful because it appears that there are many more needs than there are experts to solve them. Despite some pitfalls in this approach (the interface between the "expert" and the "software writer" is not always smooth and seamless), the benefits obtained by leveraging the experience of the expert make this approach worth pursuing.

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	Fundamental and Applied Laboratory Studies	Monitoring Manufacturing
Problems: Materials and Processing	4 issues	4 issues
Limitations and Needs	9 needs: 3 crucial 6 important	6 needs: 2 crucial 3 important 1 useful
Information and Infrastructure Issues	7 needs: 3 crucial 3 important 1 useful	3 needs: 2 crucial 1 important

Figure 1. Matrix of interfacial microchemical characterization issues and needs

27. CONDUCTING POLYMERS IN ENERGY AND TRANSPORTATION TECHNOLOGIES

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SUMMARY

The area of conducting polymers has been intensely investigated for more than a decade, with efforts focusing on materials synthesis and characterization and, more recently, on processibility and environmental stability. Only during the past few years have applications oriented research and development work been similarly emphasized—the challenge is to translate the versatility of conducting polymers into components or devices. The role that these polymers can play in energy and transportation technologies is substantial, and to this end various objectives must be achieved to produce optimized materials and devices.

An introduction to the area of conducting polymers, focusing on the importance of surfaces and interfaces in the realization of several major applications, is given first, followed by the objectives of this paper. The section that follows discusses various energy and transportation-related application areas and includes redox-type applications such as batteries, fuel cells, electromechanical actuators, displays, smart windows, and supercapacitors; EMI shielding, radar absorbers, etc.; photovoltaics and electroluminescent devices; chemical, thermal, pressure, and radiation sensors; energy transmission; and nonlinear optics. Materials processing, stability issues, and product characterization are treated in separate sections, and the last section of this paper gives a tabulated summary of research needs and priorities.

Examples of the importance of interfaces in conducting polymers include the:

- Effect of the nature of interfaces between polymer electrodes and electrolytes on rate limitation, cycle life, and cycle rate
- Effects of dimensional changes on interfaces
- Effect of interfaces on those electronic and photonic processes in which the complex interactions at interfaces need to be understood
- Surface energetics between films/coatings and substrates and the need to address the adhesion issue
- Importance of surface perfection in optical applications
- Influences of inter-particle interfaces in bulk polymers on interchain hopping and interface modification on the incorporation of dopants
- Orientation effects on crystallite interfaces

- Effect of interfaces in composites and their influence on processing techniques and percolation thresholds.

I. INTRODUCTION

This overview describes the status of conducting polymers and the role they could play in energy technologies. Focus is provided by the importance of interfaces for the applications of conducting polymers and the importance of improved abilities to manipulate the properties of interfaces, which can result in performance improvements. Years of basic research have led to the development of several products, some of which have started to reach the market, and to the fabrication of experimental, bench-scale applications. The numerous applied research results in the open literature, as well as proprietary information, need to be taken advantage of by the private sector, which has the challenge of introducing this new technology into its products and of designing applications unique to conducting polymers. In all the facets of this technology, reproducibility, reliability, and effectiveness are of importance to the potential user. There are common concerns that need to be addressed for all applications incorporating conducting polymers. Processing conducting polymers is an important aspect of materials development or device fabrication, because processing conditions often greatly affect the morphology and the surfaces of the polymer as well as interfaces. Therefore, process reliability and reproducibility is very important in any materials production-utilization scheme.

The issues of importance in the area of conducting polymers are related to materials properties and fabrication processes. Among the issues that need to be addressed are stability (of the polymer and the consequent reliability of its function in a given application), conductivity, adhesion, mechanical properties, and resistance to hostile environments, such as in automotive (under hood) and photovoltaic applications, soiling, interface properties, and performance/cost-effectiveness issues. Surface modification and passivation techniques that apply to conducting polymers and surface characterization of these polymers will be described briefly to help develop the commercialization of conducting polymer technology.

The research community has so far contributed a great deal toward the ultimate goal: the use of this technology by producing materials and bench-scale applications accompanied by a characterization effort that uses a wide variety of techniques. Systems optimization is a must for any future uses and therefore, the private sector can take advantage of the optimization process toward establishing performance windows and tolerances on processes, products, and applications produced on a large scale and thus establish a cost-effectiveness/performance correlation that justifies pursuing a specific application.

As we outline the various application areas of interest, specific questions and needs will be presented in some cases, while in other cases, general or common concerns will be mentioned. In all cases, the scientific and engineering communities need to work together to determine the most logical ways of pursuing this technology to define areas and directions for further development.

The properties of materials alone or in applications are largely influenced by intrinsic phenomena inherent in the bulk polymer. However, overall performance is influenced by materials morphology at the macroscopic (surfaces and interfaces) and microscopic scales. The former is of importance because of the polycrystalline character of conducting polymers.

In addition to the common processing effects on surfaces and interfaces in polymers in general, doping/dedoping processes add to the complexity of conducting polymers whose interfaces are affected by the diffusion of the dopant. This complexity stems from the dimensional changes that take place simultaneously as the polymer is doped or dedoped. However, advantage can be taken of these dimensional changes, as will be mentioned later.

Among the areas recommended for study in this paper are redox-type applications, shielding, and sensor applications.

II. OBJECTIVES

The objectives of this paper are (1) to outline the importance of interfaces in the technological applications of conducting polymers and (2) to improve, based on the characterization-optimization process, the methods for manipulating the properties of conducting polymers at interfaces and their stability for maintaining high performance in the various applications.

III. AREAS FOR CONDUCTING POLYMER APPLICATIONS

A. Energy Storage and Energy Conversion

The first commercialization of conducting polymers was by Bridgestone-Seiko for polyaniline button cell batteries. Such batteries use a polyaniline cathode, a lithium-containing anode, and an electrolyte in which dopant ions are stored in salt form. These rechargeable batteries display excellent shelf life with respect to charge retention and high cycle life, but suffer from inherent limitations on both energy storage density and power density. Allied-Signal researchers have shown that much higher energy storage densities can be obtained for high cycle life conducting polymer batteries if the conducting polymer is used only as an additive for an alkali-metal-alloy anode of a battery that has an inorganic cathode. Such use of conducting polymers takes advantage of the ability of selected donor-dopable conducting polymers to dramatically increase the cycle life of alkali-metal-alloy anodes. Prototype A-size batteries were constructed (using either polyacetylene or poly[p-phenylene] having about 70 W/kg capacity, compared with achievable storage capacities of about 45 W/kg for Ni/Cd cells, < 10 W/kg for the Bridgestone-Seiko button cells, and an inherent limitation of about 35 W/kg for larger polyaniline batteries of similar design.

Recent commercialization activity has also focused on the use of conducting polymers in supercapacitors. One design, commercialized in Japan, uses a conducting polymer with a compositional gradient for a metallic conductor, as well as for an electrolyte. Higher capacity, but decreased frequency response, resulted for another design of a conducting polymer capacitor, which is said to be near commercialization in Japan. This second type of capacitor is basically a high charge-discharge rate battery that uses the region of a discharge curve for a conducting polymer in which voltage is strongly dependent on dopant concentration.

Preliminary research suggests that conducting polymers provide interesting materials for the direct transformation of electrical energy to mechanical energy via the dimensional changes induced by oxidation and reduction. Conducting polymer electromechanical actuators should have more than an order of magnitude advantage over competing piezoelectric and magnetostrictive materials in work density per cycle, but they have major disadvantages in both cycle life and cycle rate compared with these alternative materials.

There is a commonality of problems that limit performance of conducting polymers in the battery, capacitor, and electromechanical actuator applications. In each case, device performance is measured in capacity per cycle, cycle rate, and cycle lifetime, and in each case, interfaces can provide important limitations on performance.

For example, cycle rate can be optimized by minimizing diffusion distances through the use of very thin electrodes. In the thin-film limit, the interface between electrode and electrolyte represents an important rate-limiting element, as well as the preferred site for chemical degradation that limits cycle life. Also, dimensional changes during redox can create interfacial stresses that limit cycle life.

B. Ionically Conductive Polymers

Research has expanded considerably in the development of solid polymer electrolytes for applications in high-energy-density batteries, supercapacitors, fuel cells, chemical sensors, and electronic displays. Specifically, advanced polymer electrolytes are key components in the development of solid state rechargeable batteries and fuel cells for transportation applications. Electrical vehicles, made possible by the development of high-performance batteries, provide one possible way to meet the demanding zero-emission mandatory regulations that will be applied in Southern California in the next few years. Similar strict environmental regulations are currently under discussion in several other states.

Polymer electrolytes offer significant advantages in comparison with liquid electrolytes. They combine in one material the function of electrolyte, separator, and binder for the cathode materials, thereby reducing the battery complexity. Polymer electrolytes cannot leak out of the battery, and they preclude the possible dangerous pressure buildups of the volatile liquid electrolytes. These characteristics make polymer-electrolyte, solid state devices safer and more adaptable to hostile environments. Moreover, polymer electrolytes can be fabricated as thin films and allow space-efficient designs of batteries or other electrochemical devices. The flexibility of polymer electrolytes also allows volume changes in the electrochemical cell without physical degradation of the interfacial contacts.

Wright and coworkers originally observed the ionic conductivity of complexes of alkali metal salts with poly(ethyleneoxide) (PEO). Armand and coworkers developed a detail understanding of the ionic conductivity of PEO and poly(propylene oxide) (PPO) salt complexes and proposed their use as polymer electrolytes in high-energy-density batteries. For the PEO-salt complexes, it has been suggested that the alkali metal cations reside in the helical tunnel of PEO, which is in a (T_2GT_2G) conformation. This structure is similar to that for the complexes between Li^+, Na^+, K^+, and crown ethers. However, PEO and PPO complexes exhibit suitably high ionic conductivity only above 100°C. In the past few years, a significant research effort has been devoted to the synthesis and evaluation of novel polymer electrolytes having the necessary structural properties to ensure high ionic conductivities at room temperature, good mechanical stability, and minimized interfacial resistance at the electrode/electrolyte interface.

Based on these goals, SRI International has recently developed unique single-ion polymer conductors with ion conductivity as high as 1.0×10^{-3} S cm^{-1} at room temperature. Single-ion polymer conductors allow greater depth of charge and discharge, and therefore better use of the electrode capacity by minimizing polarization effects at the electrode/electrolyte interface, a serious drawback of bi-ionic conductors such as PEO or PPO.

Applications of polymer electrolytes to electrochemical solid state devices will take significant advantage of the understanding of electrode/electrolyte interfacial phenomena and the development of ways to minimize interfacial resistance. With less resistance, we will achieve higher capacities, optimum cycling in polymer rechargeable batteries, ultrahigh capacity at the complex electrode/electrolyte interface of super-capacitors, higher charge/discharge rates, faster kinetics at the electrode/polymer electrolyte/catalyst interface of fuel cells, faster switching rates in electrochromic displays, and faster response times in chemical sensors.

C. Applications to Photonics

Photonics—the generation, manipulation, transmission, and detection of light—has enjoyed tremendous growth since the advent of diode lasers and optical-fiber-based telecommunications. To take advantage of propagation speeds and massive parallelism inherent in photon-based communications, information storage, and computing, fast optoelectronic and all-optical modulators are needed; devices based on highly nonlinear materials are ideal candidates for these and other applications.

Conducting polymers, and generally all π-electron containing and conjugated polymers, exhibit large third-order optical nonlinearities due to the high density and delocalization of π-electrons along the polymer backbone. For example, optical waveguide devices that exhibit all-optical switching and intensity-dependent transmission have been fabricated from several crystalline polydiacetylenes. These optical non-linearities can be further enhanced, for example, by dispersing small particles into the polymers (e.g., as with semiconductor-doped filter glasses or metal particles embedded in glassy or polymeric hosts). In addition to these nonresonant (negligible absorption) effects, conducting polymers also exhibit large, metastable changes in optical absorption (photochromism) due to the formation of in-gap energy levels associated with backbone distortions around localized photogenerated charges. These resonant optical effects can be used for optical limiting and optical information storage, e.g., as has been proposed for the conducting polymer polyaniline.

While most present applications of photonics do not appear to involve the transportation and utilities industries, the increasingly complex sensor and actuator systems required to measure and optimize the performance of automotive and aerospace vehicles and to power generation facilities, may obviate the need for optical sensors, communications, and information processing. Photonics may actually simplify some systems: for example, the central vehicle lighting concept replaces the electrical wiring, switches, sockets, and incandescent light bulbs currently used for automobile signals and headlights with a central high-intensity light source and a light-pipe distribution system, reducing complexity and weight while increasing reliability.

Most of the nonresonant nonlinear optical effects mentioned require high optical intensities (0.1 MW/cm^2) and long optical path lengths (of the order of 1 cm) to be useful; fortunately, the optical fibers and planar waveguides used in coherent optical communications provide these conditions. Surfaces and interfaces clearly play an important role in such devices, because it is imperative to reduce the optical losses resulting from scattering by crystallites, cracks, or other defects in the surface and near-surface regions of the waveguides. As yet unknown is the role of strain at the waveguide boundaries in affecting the polymeric structure and thus the optical nonlinearity.

D. Electroluminescent Devices

Another photonic application of conducting polymers is the generation of light through electroluminescence. The Cambridge group first demonstrated that diodes using semiconducting poly(p-phenylene vinylene) can emit visible light when reverse-biased current is passed through them. The spectrum of the emitted light matches that produced from photoluminescence, suggesting that the electrons and holes injected from the electrodes combine to form neutral excitons before decaying to produce light.

Subsequent studies have achieved higher light emission efficiencies through the use of metallic elements having lower work functions in the electron-injecting electrode, as well as through chemically-induced enhancements in electron mobility in the polymer layer. Surface characterization and modification are clearly as important in conducting polymer-based electroluminescent devices as they are in their inorganic predecessors.

E. Applications in Displays

Conducting or electroactive polymers exhibit dramatic color changes associated with the chemical, electrochemical, or optical doping of the polymer backbone, leading to self-trapped states that induce new electronic levels in the semiconducting bandgaps of these materials. For example, thin films of the insulating leucoemeraldine form of polyaniline are colorless, while electrochemical oxidation to the conducting form produces green films, and further oxidation yields insulating blue films. The colors produced can be quite different for other families of conducting polymers, depending on the size of the bandgap as well as the solitonic, polaronic, or bipolaronic nature of the species responsible for charge storage. Moreover, the ability to attach to the polymer backbone a wide range of derivatizing molecules allows color tuning within a particular family.

These electrochromic changes permit the construction of optical displays, windows, and light valves. Control of the electrochemical potential of the conducting polymer by an individually addressable electrode array can be used to produce a flat-panel display. Individual conducting polymer electrochemical cells have exhibited submillisecond optical switching times, sufficiently short for display applications. The transportation and utility industries could be greatly impacted by the use of so-called "smart windows"—conducting polymer/electrolyte/counterelectrode sandwich cells—to lower the solar heat load on automobiles, aircraft, office buildings, and homes.

Other automotive applications of electrochromics include variable-transmission sunroofs and variable-reflectivity rear-view mirrors. In these window applications, the time required to switch from a transparent to an absorbing state is less critical. Electrochromic windows could also be used in various other non-imaging applications such as in light valves in central lighting systems.

Central interfacial issues include the electrochemical polymerization or the spin- or spray-coating of very uniform, adherent polymer films on conducting glass electrodes. Critical to the success of imaging applications is the absence of haze due to scattering from crystallites or surface imperfections in the conducting polymer. The long-term stability of the polymer-electrolyte/counterelectrode sandwich against delamination or more subtle performance degradation due to the accumulated effects of doping-induced strain is also important. Studies of the stability of conducting polymer films against solar-radiation-induced photochemistry are also important, particularly given the facile photoproduction of long-lived doublet and triplet spins in many of these materials.

F. Electromagnetic Shielding

The large doping-induced changes in the complex dielectric permittivity of conducting polymers extend from the ultraviolet and visible regions of the electromagnetic spectrum, through the microwave and radio frequency regimes, and down to direct current (DC). Doped conducting polymers such as polyaniline, polythiophene, polypyrrole, and polyacetylene possess microwave loss factors that compare favorably with the inorganic materials now used commercially for shielding of electromagnetic interference (EMI). Conducting polymers may provide significant advantages in EMI applications given the wide variety of ways they can be used. Coatings can be applied by electrochemical or solution techniques to the object to be EMI shielded, or the object itself can be formed from materials that incorporate conducting polymers (even at low loading levels) in the form of blends, composites, or interpenetrating networks. For example, EMI shielding of lightweight electronic equipment is possible. Electrochemical conversion between the doped and undoped forms of the conducting polymer allows the EMI shielding or screening to be switched on and off at will, a potentially useful feature in some applications.

The utility of conducting polymers in electromagnetic shielding extends to the DC limit. Even relatively low conductivity, partially-doped conducting polymers can be used in antistatic applications. The wide range of processing techniques and processed forms can provide many useful materials: textiles for antistatic clothing or mats, as well as conducting coatings or composites for the entire fuel line in vehicles—fuel tank filler neck, gas tank, fuel line, and fuel filter. Static dissipation applications in the microelectronics industry include polyaniline films for reduction of charging in electron beam lithography.

The flexibility afforded by control of the derivatization and doping level of various conducting polymers allows the production of potential low-emissivity window coatings transparent in the visible, absorbing in the near-infrared, and transparent in the mid-infrared. The emissivity could be controlled via electrochemical techniques to allow tuning of the radiative properties of the windows.

G. Energy Transmission Applications

Research efforts in the last few years focused on increasing conductivity and anisotropy in conducting polymers by increasing chain orientation and chain perfection using various techniques. Some of these techniques led to the synthesis of, for example, polyacetylene, whose room-temperature conductivity parallel to the orientation direction is near that of copper. Other conducting polymers have provided chain direction conductivities that are about an order of magnitude lower than those reported for polyacetylene.

Advantage might be taken of the high conductivity and high anisotropy in electrical transmission wiring, particularly in aerospace applications in which weight is a critical issue. Oriented polyacetylene with a conductivity of the order of 10^5 S/cm, a capacitance of few pF/m and an insertion loss (attenuation) of < 0.1 dB/m would perform as a good transmission wire for some low current applications. However, the poor environmental stability of this particular polymer would require an insulation that would act as a good oxygen barrier because of the reactivity of the polyacetylene in air. Also, stable n-type dopants that provide high electrical conductivities need to be developed.

Energy transmission applications will become a reality only if the thermal stability of polyacetylene is improved to the same extent that it has been in other conducting polymers. These applications require more development work to find adequate processing techniques that would yield highly conducting fibers of polyacetylene. Other polymers, such as poly(phenylene vinylene), whose conductivity is approximately 10^4 S/cm, have been processed in the form of films and fibers. However, conductivities need to be higher for an efficient signal transmission in wiring applications in which signal insertion loss and return loss are critical. With a density of approximately one-sixth that of copper or copper alloys, conducting polymer usage in wiring applications could result in major weight savings.

Conducting polymers in the form of composites (with lower conductivities) could be used in ignition cable applications if the material is thermally stable in high-temperature environments.

H. Sensor Applications

Because conducting polymers undergo dramatic changes in electrical and optical properties on doping, dedoping, and dopant compensation, conducting polymers provide unique materials for sensor applications. For example, dopant-induced changes in polymer conductivity can readily exceed thirteen orders of magnitude—thereby providing the basis for highly sensitive indicator devices.

Remotely readable, in-box indicator devices for product monitoring during shipment have been patented by Allied Signal. These indicator devices result from the combination of conducting polymer technology with the commercially available technology of radio frequency and microwave frequency antitheft devices. Device operation depends on the coupling of conducting polymers with the antennae of the antitheft device to provide a remote, readable signal that measures the effect of selected ambient variables on the conductivity of a conducting polymer. The antitheft targets and hand-held transmitter and receiver needed for this application are inexpensive (about $0.03/target and $300 for the remote monitor. Additionally, the targets can be quite small, about one-in. square film-like devices.

Using various device designs, a variety of indicator devices have been demonstrated. The remotely readable devices include time-temperature indicators, temperature limit indicators (freeze and defrost), humidity indicators, irradiation dosage indicators, mechanical abuse indicators, and chemical release indicators. Such devices can be especially useful for applications in the transportation industry's handling of products, which can be adversely affected by environmental factors during shipment. The device can be located in the shipping container so that both product and indicator are exposed to the same environment and can be remotely read without opening this container.

Suitably designed devices respond to the effects of ambient variables in the same way as the ambient variables affect product quality. Successful design of such devices critically depends on knowledge of the effects of interfaces on the transport of doping agents and/or dopant compensation agents to the conducting polymer.

Conducting polymers are generally obtained by doping conjugated polymers with various electron donors or acceptors. Therefore, exposure of a polymer in its undoped state to one of these dopants, particularly electron acceptors, increases its conductivity to a level that depends on the amount of exposure to the dopant. In this respect, these polymers could be good sensors for halogens, Lewis acids, and protonic acids in their vapor phase or in solutions. Such applications could be useful for detecting trace amounts of these materials in working areas, in disposal areas, and in shipping.

Because conductivity is thermally activated in conducting polymers, these polymers could be used in thermal sensing devices. Because the activation energy varies with the doping level, polymers can be tailored to fit specific thermal sensing needs, based on the temperature increments to be monitored. Also, the conductivity of conducting polymers varies with pressure. This variation is influenced by morphology of the polymer, inter-particle resistance, and temperature.

For their semiconducting or undoped states, conjugated polymers respond to various radiations by an increase of their resistance. On removal of the radiation source, the resistance returns to its initial value. Therefore, conducting polymers can be good candidates for incorporation in radiation-monitoring devices relevant for the monitoring of radioactive waste storage and transportation.

IV. MATERIALS PROCESSING

Conducting polymers can be obtained and processed in various forms, some of which are outlined below.

A. Films and Coatings

Highly conductive polymers such as polyacetylene, poly(p-phenylene), polypyrrole, etc., are intractable powders in their doped conductive form. Most of these polymers can, however, be produced by electrochemical oxidation in appropriate electrolytes as freestanding films with useful electrical and mechanical properties. Thus polypyrrole films are produced commercially under the trademark Lutamer®

by BASF in Germany. Also, polyaniline, which is produced under the tradename "Versicon" by Allied-Signal Inc., can be solution-processed in either film or fiber form from either doped or undoped states.

Chemical and electrochemical polymerization of pyrrole and aniline can be conducted on support films such as polyvinyl alcohol), poly(vinyl chloride), polyacrylonitrile, polycarbonate, and others to yield composite structures combining the physical properties of the support structures with the electrical properties of the conductive polymer. Such products are commercially produced by Bayer in Germany and several companies in Japan.

A special in situ polymerization of pyrrole and aniline has been reported on materials having a large surface area such as membranes, textiles, or fillers (mica, clay, etc.). Commercial products based on polypyrrole coated textiles (fibers, yarns, and fabrics) are available in the United States under the trademark Contex™ from Milliken & Co. Products based on coated fillers are available from Cookson Inc. in England. These products show very uniform coherent coatings of conductive polymers around fibers and, in the case of fillers, particles. Similar to the properties of coated films, the coated textiles combine the basic mechanical properties of the substrate fabric with the electrical properties of the conductive polymers. In contract to the case of coated films in which a surface resistance of only several thousand ohms per square can be attained, textiles with a sheet resistance as low as several ohms per square can be produced.

Dispersions of polypyrrole and polyaniline suitable for producing coatings on various substrates have also been obtained. Commercial products of this nature have been offered in the United States by Polaroid and recently by Solvay in Belgium.

Another approach to achieve conductive polymers suitable for films and coatings is the synthesis of a tractable intermediate polymer that can be transformed by heat or other reaction into the intractable conductive polymer. Thus coatings or films are produced from the soluble or meltable intermediate and later transformed into the conductive form.

Soluble conjugated polymers can, however, be produced by the incorporation of often bulky side groups into the monomers. Such incorporation of side groups usually lowers the specific conductivity of such compounds. Solubility of polypyrroles, polythiophenes, polyanilines, and other polymers can be achieved by this method, and even water soluble products have been reported. Most of these products, however, are only soluble in their undoped form and have to be doped after the coating operation. A product of this nature is the polyalkylthiophene produced commercially by Neste Corporation in Finland.

Conductive coatings are usually produced in layers less than 1-µm thick. A deterioration of the electrical properties may be reasonably anticipated if the coatings are exposed to harsh environments. This deterioration may be on the microscopic level, such as formation of cracks and interruption of the continuity of the coating, or on the molecular level, such as disruption of the conductivity by oxidation or substitution. In many cases, the deterioration of the electrical properties has to be prevented by protective coatings or other encapsulations of the conductive polymer. There are, however, applications in which a limited high-temperature stability is sufficient for a commercial use, for instance, in static dissipation in which a difference in conductance even of several magnitudes, may be immaterial. In other applications such as in generators, motors, and transformers in which semiconducting materials are needed to eliminate certain side effects such as eddy-currents, performance with minimum variations under severe conditions of high temperature and high electric field are needed over a period of 50 years. Present conductive polymers are far too unstable for such applications at the present time.

New possibilities may also be offered through the use of multilayer conductive structures. Transportation and utilities technology areas that will be impacted by these structures include optical films (e.g., optical waveguides), protective layers (coatings and encapsulants), sensors, transducers, modified surfaces (adhesion, friction, wear, and lubrication, as well as biologically and chemically active substrates), membranes, microlithographic materials and modified electrodes and electronic devices. The potential for spin-offs to other technology areas is enormous.

Of particular interest are organized molecular assemblies (OMAs), which are thin-film arrays that can (via the influence of the substrate) possess cooperative properties different from the individual molecular components. There are a number of key scientific principles operating in molecular films that we do not understand and that prevent us from developing and using these structures. A dominant scientific issue is understanding interactions at the OMA-substrate interface, between the chains, and at the ambient interface. To gain this understanding, improved quantitative methods are needed for characterization, particularly of film defects. Additional needs include theories relating surface properties (e.g., wetting) to surface molecular structure, synthetic protocols to make highly patterned, multifunctional surfaces, and controlled pore size and pore distribution films.

B. Conducting Polymer Composites

Conducting polymer composites with insulating polymers provide a variety of application possibilities, especially in EMI shielding and electrostatic charge dissipation. Major advantages in processibility and/or achievable conductivities result for such composites in high performance applications (such as EMI shielding) compared with the case of conventional carbon black or metal-filled composites. For example, conductivities of 0.1 S/cm are achievable with difficulty for carbon black composites and are too low for use in high-performance EMI shields, while available polyaniline composites have sufficiently high conductivities (about 1 S/cm and above) that such composites are quite attractive for EMI shields. The EMI shielding application in housings is especially important for preventing electromagnetic interference for communications, computational, and transportation equipment.

A special advantage of the conducting polymer is the achievement of percolation at near zero loading levels for gel-processed polymers and at less than 8% for melt-processed polymers. The performance of such composites is strongly dependent on interfacial effects, such as interparticle contact resistances and the occurrence of percolation. Advances in understanding the chemical and structural nature of interfaces and the development of improved methods for modifying these interfaces are expected to provide further performance improvements.

C. Adhesives

The existence of readily derivatizable polymers possessing high conductivity suggests the potential for obtaining conducting polymer adhesives. For example, polyaniline derivatives have been developed as thermosetting resins for aerospace applications. Other applications include that proposed by the Ohio State University group for microwave welding of structural polymers using conducting polymers in film, composite, or powder form applied to the interface of the objects to be jointed; the strong microwave absorption of the conducting polymer causes local heating and flow at the interface. A better understanding of the interfacial processes involved—interdiffusion, entanglement, and chemical cross-linking of the polymer chains—may help optimize interfacial properties.

V. LONG-TERM PERFORMANCE AND STABILITY OF MULTILAYER CONDUCTIVE THIN-FILM STRUCTURES

The possibility of preparing inexpensive, lightweight structures of conducting materials into configurations with unique electrical properties depends critically on successfully addressing key research issues such as stability, durability, intermolecular interactions between layers or phases, purity, bonding, structure, defect concentration, and interface definition.

Widely available materials must be identified, certified, or in some cases, developed specifically for use in conducting structures.

Some of the important parameters, physical properties, and technologies required for conductive polymers in these structures include the following:

- Conductivity and its temperature-dependence in low- and high-temperature regimes
- Dopants used to obtain conductivity
- Environmental and chemical stability in air and H_2O
- Thermal stability
- Commercial availability
- Preparation, processing, and handling
- Processibility and deposition methods
- Mechanical properties, including coefficients of expansion and stability after repeated temperature cycling
- Adhesion to inorganic and organic materials
- Contact resistance to adjacent layers
- Traceability with varying topographies of different adjacent materials.

Two major impediments to the use of conducting polymers—poor environmental stability and processibility—have been considerably improved in recent years through the exploration of the following routes:

- Polymer composites
- Electrodeposition
- Ion implantation
- Solution processable systems
- Chemical vapor deposition.

However, further exploration and a more detailed understanding of mechanistic and kinetic aspects of these processes are needed.

The study of degradation (mechanism/kinetics) and stabilization of multilayer conductive structures will be crucial in improving durability of products and in predicting lifetime accurately. The primary focus of degradation/stabilization studies should relate the decline of conductivity to both external stresses (e.g., thermal cycling, photon flux, humidity, O_2, or pollutants including synergistic effects) and internal stresses (e.g., interdiffusion and mismatch in mechanical and chemical properties).

VI. PRODUCT CHARACTERIZATION

We encourage developing both new macroscopic and microscopic methods and modification of existing techniques that will make materials and interface behavior more easily accessible. Problems and constraints in this regard are expected to be similar to the ones experienced with other materials. Of particular interest is the dependence of the electrical properties for conductive layers that are only a few monolayers or less in extent. Relative enhancement of interfacial molecular properties (structural and dynamic) as opposed to molecular bulk properties is expected to be of great interest and importance. It will also be important to understand exactly the meaning of the experimental parameters measured or cited for films of various thicknesses. Characterization tools may have to be specifically designed for thin multilayer films.

The question of composition is clearly more complicated for layered materials than it is for bulk samples and will tend to be more subtle, e.g., concentrating on how composition varies with position (either in-plane or perpendicular to the plane). Intramolecular structural issues will center around how bonding occurs at a surface or interface, while structure on the supermolecular size scale will tend to address how orientations are correlated over dimensions greater than the few molecular diameters.

Diagnostic techniques and methodologies (e.g., FTIR-RA, XPS, SIMS, ISS, GPC, ellipsometry, surface plasmon resonances) need to be further developed and improved to investigate relevant research issues in conducting multilayer stacks, such as adhesion, delamination, interdiffusion, changes in interface composition, and degradation of polymers. Unfortunately, a thin-film probe with the power that NMR has for bulk samples is still not available.

Attention should also be paid to the issue of sensitivity and the effect of the characterization probe on the characteristics of the thin-film structure. The ability to provide in situ information is of utmost importance, because the chemistry, microscope organization, and thus the function of the surface-bound species in OMAs can be very dependent on the specific chemical environment in which they are situated.

VII. SUMMARY OF TECHNICAL GOALS AND R&D NEEDS

A summary of R&D needs is proposed in Table 1 as a guide for future efforts.

Table 1. Summary of Technical Goals and R&D Needs for Conducting Polymers

Goals	R&D Needs
A. Increase achievable electrical conductivity.	Develop processes that decrease interparticule resistances and induce percolation of crystallites with optimal orientation. Improve orientational order, e.g., by oriented substrates.
B. Develop conducting polymers with improved conductivity without decreasing convenient processibility.	Develop the understanding required for the manipulation of interparticle interfaces so as to achieve high conductivities in bulk polymers and low percolation thresholds in composites.
C. Achieve improved environmental and thermal stability.	Explore the application of surface modification techniques for improving thermal and environmental stability of coatings and multi-layer structures. Apply passivation techniques known for other polymers.
D. Develop processing methods suitable for the various materials and applications.	Develop substrates for thin-film applications. Develop dispersion techniques to achieve high conductivities at low percolation thresholds in composites. Improve solubility and melt processibility of the bulk polymers with high molecular weights.
E. Optimize ionic conductivity and mechanical properties of polymer electrolytes.	Find ways to minimize interfacial resistance between the polymer electrolyte film and the electrode.
F. Optimize substrate surfaces in which interface properties are critical for good performance in device applications.	Achieve control of the polymer synthesis and the subsequent surface treatment necessary for a given application.
G. Achieve transparent conducting polymers.	Improve thin-film fabrication and develop materials with suitable bandgaps.
H. Achieve strong adhesion of conducting polymers onto various substrates.	Develop an understanding of surface energetics.
I. Fabricate polymers with useful mechanical properties, such as high tensile strength and flexibility.	Determine the of effect of increased molecular weights and molecular weight distribution on the mechanical properties.

28. PHOTOELECTROCHEMICAL SYSTEMS

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SUMMARY

Photoelectrochemical systems encompass numerous applications involving semiconductor/electrolyte interfaces. A major goal has been solar energy conversion. Double-digit efficiencies have been reached with two different forms of semiconductor-electrolyte photojunction, directly excited or dye-sensitized. Impressive performance with even polycrystalline semiconductor substrates is attainable in these devices and makes them promising in photovoltaics and photoelectrosynthesis for efficiency and cost. Achieving improved stability and further advances in output and economics depend on further progress in understanding and modifying solid/liquid interfaces. Related developments have produced numerous spin-offs of substantial importance to solid state devices, processing technology, and surface chemistry. Further progress toward significant applications of interest to utility, electronics, and transportation industries, in energy conversion, and toward a host of specialized opportunities from sophisticated etching of microstructures to water purification, requires a serious effort to support and strengthen the fundamental underpinnings of the field. These needs are categorized in the conclusion of this overview.

I. INTRODUCTION

Photoelectrochemistry, for our purposes, involves systems in which light excitation at a semiconductor-electrolyte junction causes charge separation and transfer to occur, with consequent chemical reaction at the interface. Light to electrical energy conversion may be one outcome, when the junction is coupled into a cell to complete a circuit and has held the pivotal attraction. However, the chemical aspects lead to many other applications of increasing importance. Interest in phenomena at semiconductor-electrolyte junctions is historically coincident with the invention of the solid state photovoltaic solar cell. Both areas have advanced from the base of understanding in solid state physics. A junction coupled to bulk phases exists in both solid state and solid-liquid devices, and the study of these interfacial regions has been an important theme for physics and chemistry in the last 40 years.

In the 1970s, the experiments of Fujishima and Honda [1], showing the feasibility of solar production of hydrogen fuel in a semiconductor-electrolyte cell, and Gerischer's basic concept [2] of a power-producing semiconductor-photoelectrochemical device led to rapid progress in the direction of energy conversion. With parallel growth in understanding of the active interface, the field has also evolved widely, and there have been a multitude of imaginative extensions outside of energy problems. We will briefly outline the scope of these developments and summarize the research needs required for further translations into effective technology.

We treat the subject in five parts: Energy Conversion; Fabrication of Interfaces and Structures; Characterization; Synthesis, Detoxification, and Degradation; and Fundamental Issues. Funding of related research has been reduced since the early 1980s along with the diminished overall effort toward solar alternatives. Some of the promise for solar energy conversion has been dulled by generally unresolved long-term stability issues attributable to the chemistry at the solid-liquid junction. Yet it is important to realize that the energy conversion research has been synergistic to the numerous other applications these efforts have spawned. We conclude with a list of needs for research, standards, and methodologies in this field that must be met to have substantial impact on surface processing and related technologies.

II. ENERGY CONVERSION

A. General Features

An illuminated photoelectrochemical (PEC) cell bears a formal resemblance to a traditional Schottky barrier photovoltaic (PV) device, with the metal layer contacting the semiconductor replaced by an electrolyte containing an appropriate redox couple. For both PEC and PV junction devices, light above bandgap energy excites carrier separation in the semiconductor, driving electronic charge (electron or hole, for p- or n-type, respectively) into the semiconductor bulk. Translating this into a current in a PEC requires charge transfer chemistry to occur both at the semiconductor electrode surface and at a second surface, or counterelectrode. The solid/liquid interface and the coupled chemistry impact cell function, design, and applications. Both striking opportunities and some inherent disadvantages for long-term energy conversion result, when compared to the PV counterparts.

A semiconductor/electrolyte junction forms spontaneously and has continuous contact between the two phases. With excitation and charge collection at such junctions occurring close together, solid/liquid devices usually provide better performance with polycrystalline materials than solid state devices because a more complete junction is formed by liquid wetting the polycrystalline grains. Since the PEC electrolyte is continuously available to the active junction, the interface may be modified to accomplish stability and enhance solar to electrical conversion. Many other useful aspects of the liquid junction system follow from these features. It is of considerable importance that the semiconductor may be in the form of discrete particles. Then the photocathodic (for p-type) or photoanodic (for n-type) reactions at the semiconductor surface are carried out vicinally to the respective anodic or cathodic reactions at an electronically coupled local counterelectrode. Fuel or other synthesis products may be generated in this mode, rather than having direct power conversion through an external circuit.

Power conversion efficiencies comparable to those of solid state cells have now been achieved in a variety of photoelectrochemical cells. The knowledge base derived from these advances has furthered other applications, such as microfabrication of solid state devices, sensors, photocatalysis, and environmental improvement schemes, as elaborated in subsequent sections.

B. Light Absorption and Charge Transfer Schemes

In photoelectrochemical systems, the absorption of photon energy yields electronic energy in the form of excess electron-hole pairs in semiconductors or in excited electronic states in molecules. Without a mechanism of charge separation, this initial electronic energy would be lost as heat through recombination. Two distinct mechanisms of converting an excitation process into charge separation (currents) have been applied in designing efficient photoelectrical systems. At semiconductor/liquid interfaces, an electric field (the space-charge layer) forms at the semiconductor surface with charge/ion redistribution at the liquid interface. If the photons are directly absorbed in the semiconductor to produce electron-hole pairs, this electric field impedes recombinative processes by oppositely accelerating and separating these charges, leading to minority-carrier injection into the electrolytic redox couple and photodiode behavior. This concept of carrier generation is illustrated in Fig. 1a (for an n-type semiconductor).

Homogeneous photodriven molecular redox reactions are conceptually an alternative conduit for photoelectrochemical energy conversion, leading to photoexcited products that migrate and inject their charge into separate anodic and cathodic electrodes. However, such coupled charge separation and transport processes are too slow to inhibit recombination or other efficiency-destroying events, unless the excited molecules are directly adsorbed on the semiconductor to act as a charge mediator. In this latter dye sensitization mode, light absorption occurs in the dye, and the photogenerated majority carrier is then injected into a wide bandgap semiconductor, as illustrated in Fig. 1b.

Development of dye-sensitized semiconductors was slow because of the limited fraction of light that could be harvested by a monolayer of dye and by competitive chemical degradation pathways for the excited dye, considering the large number of turnovers of the injection process required for long-term stability. The first example of a dye-sensitized device with efficiency comparable to those achieved by direct excitation (Fig. 1a scheme) was recently demonstrated through the use of a novel high-surface-area, thin-film nanostructure of n-TiO_2 (produced by sol-gel routes), which is coated with an energetically matched trimeric ruthenium complex of high photostability and immersed in an iodide/iodine-containing electrolyte. The unusually high surface area of the transparent semiconductor, coupled to the spectral characteristics of the dye, harvests a high proportion of the incident insolation [3].

Surface stability severely limits the life of electrolytically immersed semiconductors, and photocorrosion is of particular concern. A semiconductor or dye thermodynamically well matched to the solar spectrum may be intrinsically reactive in the PEC electrolyte. These factors restrict the choice of suitable electrolytes and require inventive chemistry.

C. PEC Developments

Photoelectrochemical energy conversion is thus a hybrid field encompassing electrochemistry, spectroscopy, and solid state physics. Solar energy incident onto a variety of semiconductors can drive electrochemical reactions and result in the production of not only electrical, but also chemical or electrochemical energy. In both Figs. 1a and 1b, the photoelectrode is coupled to a metallic counter-electrode to generate electricity regeneratively, i.e., with no net chemical change. Examples of cells with high solar to electrical conversion efficiencies are summarized in Table 1.

These efficiencies approach those of more mature solid state photovoltaic devices. Efficiency may also be expressed in terms of the power saved in carrying out chemical fuel production. In one such cell, power savings for hydrogen generation at platinized p-InP have been realized by utilizing up to 12% of the incident sunlight [12].

Finally, the components of a PEC cell are analogous to those in a conventional battery and, in principle, the charge produced by the cell can also be electrochemically stored by the addition of a third

Table 1. Regenerative PEC Solar to Electrical Conversion Efficiencies

Year	Solid/Reacting Ion	Efficiency, %	Ref.
1991	nano n-TiO_2(dye)/I^-	~8	3
1990	n-CdSe/$[KFe(CN)_6]^{3-}$	~16	4
1987	n-GaAs(Os^{3+})/Se^{2-}	~15	5
1985	n-Cd(Se,Te)/S^{2-}	~13	6
1982	n-$CdInSe_2$/I^-	~9	7
1982	n-WSe_2/I^-	~10	8
1981	n-$MoSe_2$/I^-	~9	9
1981	p-InP/V^{3+}	~12	10
1978	n-GaAs(Ru^{3+})/Se^{2-}	~12	11

electrode and an appropriate separator, instead of being stored in a product fuel. Figure 2 shows one configuration of a PEC cell combining such in situ electrochemical storage with solar conversion capability to yield a continuous output that is insensitive to daily variations in illumination. The practical system shown combines a Cd(Se,Te)/S^{-2}_x based conversion half cell and a Sn/SnS storage electrode to give a single cell operating at an overall efficiency of 11.4% [13]. Under illumination (Fig. 2a), photocurrent is used partly to drive an external load and partly to reduce metal cations in the storage electrode. Then, in darkness or at low light levels, the storage compartment can take over power delivery (Fig. 2b) by metal oxidation.

D. Economic Considerations

Practical terrestrial energy conversion requires inexpensive, efficient, and stable devices. Inexpensive systems require low-cost materials, ease of fabrication, simple chemical steps, and a means of handling the chemical fuel produced, if the latter is the desired product. For any kind of photovoltaic device, synthesis of single-crystal material is often time- and energy-intensive, and the process will normally be limited to forming smaller cross-sectional area cells at high cost. A variety of techniques can provide cheaper forms of polycrystalline or amorphous thin-film semiconductors to consume relatively small amounts of material while covering large surface areas. Modes of film preparation include slurry techniques, chemical vapor deposition, casting of polycrystals, radio frequency (RF) sputtering, vacuum co-evaporation, sol-gel processing, chemical bath deposition, hot pressing, and electrodeposition, among others. These techniques have been variously used to prepare thin-film electrodes of n-CdS, n-CdSe, n-CdTe, n-GaAs, p-InP, n-Si and p-Si, and n-TiO_2 for PEC cells [3,14].

A particular advantage of electrodeposition (plating) techniques is the possibility of a one-step chemical synthesis of a semiconductor without employing a great deal of heat energy to form the eventual electrode, thus reducing the energy payback time, as well as initial cost, compared to virtually every other scheme of synthesis. Future developments in both solid state and liquid junction photovoltaics will benefit from a variety of commercial thin-film techniques being developed for materials such as a-Si:H, $CuInSe_2$, CdS, CdTe, and GaAs.

The performance of photoelectrochemical solar cells can degrade with time, typically significantly faster than is observed for solid state cells. Corrosion and passivation of the solid/liquid interface and degradation of the electrolyte can occur. Countering the degradation processes requires controlling kinetics through the photoelectrochemical interface and developing alternative stable combinations of semiconductor and electrolyte. A loss of efficiency is generally observed for polycrystalline materials compared to single-crystal forms. These losses are generally attributed to kinetic origins, e.g., recombination at grain boundaries. It is of interest that thin-film PEC structures have sometimes exhibited greater stability than single-crystal counterparts, which have better initial efficiencies. This phenomenon has been attributed to lower microscopic photocurrent density. The longest lifetime PEC device demonstrated to date, slurry-deposited thin-film n-Cd(Se,Te) electrodes immersed in modified polysulfide solutions, has operated outdoors for approximately 1 year. In this system, photoelectrode and electrolyte stability was achieved by systematic optimization of the solution composition [15]. Efficient dye-sensitized devices, with a 2-month-equivalent sunlight lifetime, have been demonstrated. This advance reflects a substantial reduction in the quantum yield to degradation reactions with Ru-based dye complexes compared with previous all-organic light absorbers.

III. FABRICATION OF INTERFACES AND STRUCTURES

Many fabrication procedures developed for PEC cells apply to other areas. Exploitation of light-induced chemistry of the semiconductor at an electrolyte junction includes surface tailoring, etching, and other manipulations of the morphology and surface composition of semiconductors. Since all of these efforts relate to the surface processing of semiconductors and to the same underlying theory implicit in our discussion of photoelectrochemical cells, they will also benefit from better understanding of the fundamentals of this technology.

A. Etching

The etching of semiconductors, with and without the action of light, is critical to the cleaning and texturing of surfaces for device fabrication and formation of geometric shapes and interconnects in integrated circuit and wafer-level technology. Covering the range from preparing uniform, smooth surfaces with low recombination velocities, through anisotropic processes for patterned pits or holes, to light-assisted drilling of vias, these applications of semiconductor/electrolyte interfaces have become familiar to modern processing. The net chemical reaction generated at any local area of a semiconductor surface by a flux of light is usually proportional to the local intensity of absorbed light. Some of the most interesting applications have been ones in which the incident light has been spatially patterned in electrolytes compatible to the accompanying dissolution chemistry and kinetics. A sampling below of some of the more sophisticated light-assisted etching techniques that have had impact on semiconductor technology illustrates the versatility of photoelectrochemical processing.

Symmetrically graded intensity has been used to fabricate lenses directly on emitting surfaces of semiconductor lasers [16], diffraction patterns from a pair of light beams have inscribed holograms [17], and laser beams of ultraviolet (UV) frequency have drilled holes in semiconductors [18], all through photochemical processes. Gratings can be made with v-grooves etched through resist patterns [19], and surfaces can be textured to be matte and nonreflective for photothermal methods, as well as for PEC or PV efficiency improvement [11]. Etching can be controlled, either through light generation of carriers or through charge injection by the redox system, under circumstances appropriate to the redox potentials and the substrate band edges in the redox medium. Many open questions remain in these areas that have to do with chemical processes (dissolution mechanisms, passivation), light channeling, and solid state diffusion lengths, charge transfer kinetics, and crystal face faceting and etch-stopping phenomena. The interactions between chemistry and solid state transport that lead to structures of extreme anisotropy and phenomena of high contemporary interest, such as luminescent processes in porous silicon, are not yet understood. Many improvements in the efficiency and reproducibility of PEC and PV converters have resulted from etching processes that provide more ideal surfaces with fewer surface states and reduced recombination.

Forming complex wafer-level structures requires demanding processing steps to carry out either anisotropic or isotropic material removal, as necessary. Both "wet" and "dry" (chemical solution and plasma etching) methodologies are required for the full range of problems, although the plasma methods are more adaptable to the anisotropic etch needs of fine line patterns. Mechanistic understanding of the wet chemical processes has lagged. Kinetic interpretation has advanced further in the study of the competitive substrate corrosion processes in PEC cells than in the area of understanding purposeful etching itself.

Commonly achieved submicron dimensions are placing greater demands on the quality of substrates as dielectric layers become thinner and breakdown mechanisms are more severely tested. This requires interpreting surface roughening from chemical treatment in much more detail than earlier technology required. Development progresses, but generally through empirical studies. The selectivity of dissolution rates for different semiconductors or alloys, as in III-V laser fabrication, is an example. Considerably less effort has been expended on systematic studies of differences between related materials, or of different crystal faces in the same pure (or alloy) semiconductor.

Significant accomplishments have been made through these sophisticated means of what amounts to micromachining of surfaces. Modeling here is difficult because of the complex interactions. Better mechanistic understanding is needed because of the diversity and attraction of the applications and the dependence of semiconductor and laser device fabrication on the control of many such techniques.

B. Deposition

Reference has already been made to the deposition of thin films by a variety of means to form semiconductor substrates for energy conversion devices. Electrochemical techniques have long been attractive for such substrate synthesis, i.e., additive processing schemes as opposed to the subtractive ones of the etching section. Large-area devices can be formed electrochemically and economically with an energy expense that is readily recoverable because the current densities and voltages of solar conversion cells in outdoor exposure and in electroplating are very much alike. Nonelectrolytic immersion chemistries are similarly attractive for economic manufacturing.

Examples of both chemical and electrochemical synthesis are plentiful, especially for II-VI compounds, but there are limitations in the device quality of materials formed. Crystallinity is sometimes achieved only with postannealing, not in the as-deposited product. The epitaxy or crystalline order that can be achieved with chemical vapor or molecular beam deposition is a problem for the solvent systems of electrochemistry. Whether efforts to improve electrochemical morphology (by such techniques as underpotential deposition to introduce epitaxy) will have broad impact is a research question. These studies can now be supported by the proliferation of surface structure and in situ techniques, such as scanning tunneling and atomic force microscopies, which have only very recently been made available.

C. Specialized Surfaces and Sensors

Because of the need in a PEC cell to improve the kinetics of the desired charge transfer step while inhibiting photocorrosion, much effort has gone into modifying surfaces by chemical or electrochemical means to enhance efficiency and stability. Modification can range from using submonolayer additions of metal ions [5,11] or depositing thin, electron-tunnelable films of surface oxides [10], all the way to forming a buried junction of a discrete metal or polymer interphase to which the solution phase is only a contact, not barrier-determining. The chemical lessons learned in improving these surfaces have also been applied to solid state PV junction devices of higher efficiency and to new sensors, as examples of interesting spin-offs.

Sensors dependent on surface interaction of liquid or gas phases with a semiconductor that alters the potential distribution or work function of the surface have been developed for a wide range of species. Work function devices with metallized semiconductors are used as hydrogen sensors, for example. The field of electrolytic sensing through changing potentials in the gate region of a field effect transistor has grown strongly during the period common to work on PEC interfaces [20]. Light addressable photoelectrochemical sensors (LAPS) [21] have been shown to be versatile and sensitive devices for a wide variety of species.

Insight into modulated structures such as quantum wells and possible new functions for them have been obtained by photoelectrochemical techniques [22]. The formation of porous nanostructures with high bandgap materials such as n-TiO_2 was earlier mentioned as critical to improving the efficiency of dye-sensitized cells [3]. Self-assembled monolayers may also be used to modify semiconductor substrate surfaces. All of these areas of surface morphology manipulation are subjects of very recent interest, and will continue to have synergistic interaction with photoelectrochemical studies.

Further credence to the need for fundamental studies is evident from the brief mention in this section of the inventive interface engineering already employed on PEC cell surfaces. There are also numerous key issues in catalysis, spatial control, selectivity, kinetics, and environmental compatibility that underlie application and need to be pursued.

IV. SYNTHESIS, DETOXIFICATION, AND DEGRADATION

As we have discussed, photoelectrochemical systems may facilitate not only solar to electrical energy conversion, but may also drive electrochemical and chemical energy processes. This concept has been productive in photoelectrochemical synthesis, production of fuels, and detoxification of pollutants in water systems. It has also contributed to our understanding of natural solar processes occurring where there are semiconductors in contact with reactible substrates.

The classic system exemplifying photoelectrochemical synthesis is water photoelectrolysis to generate hydrogen. Fujishima and Honda [1] showed that n-TiO_2 can be used to split water at about 0.1% solar to chemical energy conversion efficiency. This semiconductor has a bandgap of 3.0 eV and absorbs about 4% of the incident insolation. Other wide bandgap materials can absorb photons energetic enough for this reaction (Table 2), but they have similar efficiency constraints.

Materials with a bandgap of less than 2.0 eV are much more capable of excitation with a substantial fraction of the incident sunlight, in which 1.4 eV for a single absorber yields an optimum solar efficiency by balancing the overlap with the solar spectrum and photon energy. Materials with bandgaps near 1.4 eV may be used for hydrogen generation with concurrent electrical bias (Table 2).

Photoelectrochemical generation of products can result from photocatalysis when the reaction is thermodynamically favored, but kinetically inhibited (the synthesis of ammonia from the elements). Product formation may be driven energetically by light excitation when the reaction is uphill thermodynamically, as in most fuel-generating reactions (water splitting or various carbon dioxide reduction schemes). Goals for both types of processes include obtaining valuable products, energy savings, environmental advantage, novel routes, useful fuels, remote generation on demand, and modeling of biological pathways.

Table 2. Photoelectrolysis of Water

Year	Semiconductor*	Bandgap (eV)	Counter Electrode	Ref.
1972	n-TiO_2(c)	3.0	Pt	1
1976	n-TiO_2(c)	3.0	p-GaP (2.4 eV)	23
1979	n-Fe_2O_3(f)	2.2	Pt	24
1981	p-InP(Ru)(c)	1.35	Pt	12
1986	n-$SrTiO_3$ (doped)	~3.0	Pt	25
1986	p-Si(c)/polypyrrole	1.1	RuO_2(p)	26
1986	p-CdTe(f)	1.4	Pt	27
1986	p-InP(c)	1.35	n-GaAs	28
1988	n-CdSe(c)	1.7	—	29

* c = single crystal; f = film; p = powder

A variety of photoelectrochemical synthetic processes have been studied. Carbon dioxide or simple organics have been converted to molecules like methanol, formaldehyde, formic acid, or methane on substrates such as TiO_2 [30], GaAs and GaP [31,32], SiO_2 doped Fe_2O_3 [33], and $BaTiO_3$ [34-37]. Hydrogen and carbon dioxide have been generated from sugar, starch, and cellulose at RuO_2 and TiO_2 interfaces [38]. The conversion of Cl^- and Br^- to halogens at MoS_2 or $MoSe_2$ junctions has also been reported [39]. Numerous other examples could be cited.

Photoelectrochemical systems have been suggested for decontaminating environmental pollution or other detoxification processes. A model system has even been suggested for saline demineralization combining photoredox and membrane processes [40]. The photoassisted oxidation of oil slicks on sea water is being pursued and modeled on TiO_2 particles [41,42]. Certain noxious inorganics can be broken down on semiconductor particles. Practical developments in these areas could lead to large-scale applications.

Thus photoelectrochemical systems have value not only as energy conversion devices, but also in electrosynthesis, detoxification, and understanding and preventing light-driven degradation reactions, such as those that might occur in illuminated paints containing semiconductor pigments. We stress that the underlying kinetics and thermodynamics of particles have a close relationship to the photoelectrochemistry already discussed. However, there are many special circumstances to be considered, among which are catalyzing the surfaces of small particles for both anodic and cathodic reactions, the consequences of generating products in close proximity, and quantum confinement effects, in small enough particles, that shift bandgaps, band edges, and light absorption characteristics. These generate theoretical problems for the underlying science above and beyond those of macrosized semiconductor electrodes.

V. CHARACTERIZATION

A. Introduction

The characterization of photoelectrochemical cells needs to serve at least the significant functions of

- Developing standards and testing procedures for PEC devices
- Establishing the surface, interface, and bulk properties of semiconductor materials
- Developing general techniques that can be used to analyze other related systems.

Standardizing the testing of PEC devices is necessary to provide a consistent means of comparing data on their efficiency and stability, and on other quality measures. Accelerated test procedures would be preferable, although the complex nature of the total cell complicates such considerations. On a fundamental level, techniques are necessary to characterize the nature of surfaces, interfaces, and bulk materials. Both electrochemical and nonelectrochemical techniques are required. An important consequence of progress in interfacial and bulk characterization is that these techniques can be applied to other systems. Methods that can be applied in situ have received increasing attention and have obviously great value in electrolyte systems.

B. Standardization of Testing Procedures

Although PEC engineering efficiency, which is nominally the straightforward measure of the ratio of electrical power out/light power in, there is, nonetheless, a strong need for standardization of testing procedures. Taking a maximum voltage-current product from a cell output is routine, but whether 2- or 3-electrode configurations are used (all or part of the resistive loss accounted for, respectively), and whether cell engineering or counterelectrode placement are realistic, are some of the factors that impact on the final percent of efficiency claimed. The spectrum of the light source, as well as the absolute power level, is also critical and has effects varying with the semiconductor bandgap, action spectrum, and solution absorbance. There are typically more variables in the measurements of a PEC device than of a PV device. Measurement in actual sunlight or with solar simulators is desirable, but there are intensity and spectral effects to be considered for specific conditions, and standardization is required for effective comparisons. For the most part, stability data can be obtained with laboratory light sources as long as there are no special wavelength-sensitive degradation mechanisms. In one such case, photon energies that can excite the wide bandgap semiconductor in dye-sensitized cells will lead to greatly increased dye degradation.

Accelerated testing is an important goal, especially to determine the long-term stability of PEC cells. Reasonable means of stressing the cells for this purpose need to be evaluated. For example, an enhanced level of light intensity may change the degradation mechanisms and, consequently, the lifetime estimation.

C. Analysis of Surfaces, Interfaces, and Bulk Properties

Many techniques have been used in the characterization of surface, interface, and bulk properties of PECs. Historically, the determination of bulk parameters such as minority-carrier lifetimes and carrier diffusion lengths have been well established from solid state physics, and certain techniques, such as Mott-Schottky plots, were used initially for electrolyte junctions. During the last 10 years, a number of novel techniques have been developed for the characterization of electronic, electrochemical, and chemical processes at semiconductor/electrolyte interfaces. These can be grouped under electrochemical, solid state, and nonelectrochemical methods.

Table 3 contains a summary of techniques currently available for the characterization of semiconductor surfaces, the interfacial region, and bulk properties of both phases. Further discussion is beyond the scope of this chapter. Combining the methods listed in Table 3 with the many forms of in situ optical spectroscopies and techniques such as scanning tunneling and atomic force microscopy, gives the experimenter powerful tools for understanding the fundamentals processes in PEC cells. The diversity of materials introduces the question of availability to individual investigators and the encouragement of cooperative work that compares different complementary techniques.

D. Needs

The dynamic nature of semiconductor/electrolyte interfaces requires characterization methods sensitive to kinetic parameters. The properties of PEC cells are such that techniques should be sensitive to bulk, interface, and surface processes arising from the potential drops in these regions. Although a wide range of analytical tools has been identified above, there still remains a need for improved techniques to characterize many aspects of these interfaces, particularly those sensitive to interfacial dynamics. Processes related to passivation, surface damage, and surface stability are examples in which improved characterization techniques would be of considerable benefit.

The complications of electrode processes, however, can be reversed to advantage in many cases. The electrochemical interface can be used as a temporary contact to characterize bulk and interfacial properties of semiconductor materials. Such flexibility is unique to the semiconductor/electrolyte interface.

Table 3. Characterization Techniques for PEC Cells and Components

I. Techniques at Semiconductor/Electrolyte Interfaces.

These techniques involve the use of an electrolyte as a means for voltage perturbation and current collection. Since the electrolyte phase is removable, these techniques may also be used for the characterization of solid state structures and devices [43].

Technique	Application
Photocurrent Spectroscopy—measurement of photocurrent as a function of wavelength, intensity, electrode potential, and electrolyte composition.	Determination of surface and bulk properties of semiconducting and insulating materials (e.g., quantum efficiency, bandgap, inter- and intra-band transitions, structure, localized states, etc.), characterization of processes such as recombination, trapping, photocorrosion, tunneling, etc.
Photocurrent Imaging—measurement of the spatial distribution of photocurrent (or photovoltage) as a function of wavelength, intensity, electrode potential, and electrolyte composition [44]. Resolution ~ 2 μm.	Identification of spatial distribution of defects, grain boundaries, secondary phases, surface damage, sub-bandgap states.
Capacitance/Mott-Schottky Analysis—measurement of space-charge capacitance as a function of band bending (voltage). Usually a single frequency measurement.	Determination of dopant concentration and flat band potential; in some cases, interband states may also be measured.
Carrier Depth Profiling—sequential capacitance measurements and photoetching.	Determination of dopant concentration as a function of depth into the material.
Electrochemical Photocapacitance Spectroscopy (EPS)—measurement of capacitance or full frequency impedance response under sub-bandgap illumination [45].	Determination of density of deep-level states and rate of trapping.
Electrochemical Impedance Spectroscopy—measurement of electrode impedance as a function of frequency (typically 10 kHz-1 mHz) under illumination as a function of wave-length, intensity, electrode potential, and electrolyte composition.	Analysis of kinetics of photoprocesses in space-charge and double layer regions; electron transfer to electrolyte; bulk and surface recombination; trapping at surface states, etc.
Photoacoustic Spectroscopy (PAS)—measurement of acoustic signal generated by light absorption [46].	Characterization of processes such as radiationless recombination.

Table 3. Characterization Techniques for PEC Cells and Components (Concluded)

Technique	Application
Intensity Modulated Photocurrent Spectroscopy (IMPS)—measurement of the alternating current (AC) response to a modulated photon flux as a function of direct current (DC) intensity, wavelength, electrode potential, and electrolyte composition. Alternatively, the frequency dependent quantum efficiency may be determined from photocurrent transient data [47].	Frequency domain analysis of relaxation of photoprocesses in terms of the frequency-dependent quantum efficiency. Kinetic analysis of electron transfer, recombination, trapping, etc.
Time Domain Transient Analysis—measurement of the time dependent photocurrent (or photovoltage) response to a short photon pulse (1 ps - 1 μs). Measurements may be performed under open circuit conditions across a load (two-electrode cell) or with constant band bending (three-electrode cell) [48].	Analysis of the kinetics of bulk and surface recombination, electron transfer via surface states, charging of the space-charge region, relaxation of the band edges (two-electrode cell). For ultrafast pulses, processes such as carrier generation may be investigated.
Maximum Power Spectroscopy—the maximum power output of a PEC or PV device is measured from the cell response to a small amplitude AC voltage perturbation as a function of light intensity and wavelength. This technique can also be used for the spatial distribution of the maximum power output by scanning a focused laser beam [49].	Identification of regions of efficiency losses in PEC and PV devices. Analysis of loss mechanisms.

II. Techniques at Solid State Junctions.

These techniques were developed for the characterization of solid state structures and devices.

Technique	Application
Electron Beam Induced Current/Photon Beam Induced Current (EBIC/PBIC)—measurement of current induced by focused electron or photon beam excitation as a function of distance from a junction. EBIC may be carried out in a scanning electron microscope with a resolution of ~ 0.1 μm.	Determination of minority-carrier diffusion length as a function of position.
Open-Circuit Voltage Decay—measurement of the rate of decay of the open-circuit voltage in response to minority-carrier injection.	Determination of carrier lifetimes.
Transient Capacitance Measurement—measurement of the capacitive time constant in response to a voltage step at a reversed biased semiconductor/insulator interface. Spatial resolution obtained by deposition of metal dots on the insulating layer.	Determination of carrier lifetimes.

VI. FUNDAMENTAL ISSUES

The previous sections have covered a variety of applications of semiconductor/electrolyte interfaces and their characterization. The areas considered for enhanced support are investigation of the photoelectrochemical conversion of light to electrical and chemical energy, investigation of electrochemical and photoelectrochemical means for the fabrication of interfaces and structures, investigation of characterization techniques that employ or pertain to semiconductor-electrolyte interfaces, and investigation of photoelectrochemically driven reactions such as chemical synthesis and detoxification of hazardous wastes. Success in these target areas requires a parallel effort for study of the theoretical underpinnings, termed here the supporting fundamental issues. An overall physical and chemical description for photoelectrochemical systems already exists. Transferring this description to specific systems will require supporting further research in promising areas defined by these investigations.

A. Introduction

The critical components of a PEC (see, for example, Figs. 1a and 1b) are the semiconductor, the electrolyte, and a counterelectrode. Electrical connection is made to the semiconductor through an ohmic contact, and illumination can be provided through the electrolyte or the ohmic current collector. Developing comprehensive models for this system requires that the physics governing the optical and electronic processes within the semiconductor be coupled to the electrolytic processes that govern the electrolyte. A unique aspect for the development of comprehensive models for photoelectrochemical cells is that the models must account for the coupling of processes that take place in regions of vastly different scale. The thickness of the electrically neutral region of a semiconductor depends on the dimensions of the electrode and may be of the order of 100 μm. The space-charge region in the semiconductor may be of the order of 0.1 μm. The electrolytic analogy to the space-charge region is the diffuse part of the double layer, which may extend 0.002 μm, but is typically of the order of ionic dimensions in more concentrated electrolytic solutions. Concentrations vary in an electrically neutral region that may extend 100 μm, and, outside this region, current and potential are governed by Laplace's equation.

The equations for convective and diffusive transport of species though the electrolyte are well established, as are those that govern the solid state behavior of the semiconductor. The interface between the semiconductor and electrolyte, however, is not as well understood. Although the semiconductor characteristics play a significant role in determining the performance of photoelectrochemical cells, further success will require a mechanistic understanding of the role of electrolytic species. The unresolved issues tend to center on physical properties that determine the interaction between the electrons and holes in the semiconductor and the ionic species of the electrolyte. Because certain aspects of this system are well understood, careful experimental design can be used to isolate the unknown features. For example, use of a rotating ring-disk electrode, for which the fluid mechanics and mass-transfer characteristics are well defined, can be combined with concomitant control of the light flux. The influence of interactive variables can be individually distinguished through experimental designs that allow application of mathematical models for interpretation of results.

B. Areas for Research

Fundamental research in the area of energy conversion should improve the understanding of the semiconductor-electrolyte interface and provide a data base for electrolyte modification. Work is needed in several coupled areas:

- Heterogeneous reaction mechanisms. The sequence of bond breaking is critical to understanding the way facets are formed, for example, in the photoelectrochemical fabrication of small devices. Passivation phenomena and charge transfer kinetics are important in energy conversion and chemical synthesis as well as in fabrication. The understanding of the manner in which the surface may be stabilized against corrosion and the manner in which self healing can occur will also depend on knowledge of kinetic mechanisms.

- Polycrystalline surfaces. We have mentioned that a significant difference between solid state and photoelectrochemical solar cells lies in the relative ease of forming an interface with both crystalline and polycrystalline materials that is accessible for characterization by external probes. Although some empirical rules have been established to relate the photoelectrochemical performance of polycrystalline materials to single-crystal counterparts, development of a better understanding of morphological effects is critical. Grain boundaries are associated with increased recombination losses, reduced current densities, and increased effective surface area. Solid state diffusion is enhanced in grain boundaries.

- Double layer structure. Many of the techniques used to characterize the electronic structure of semiconductors rely on measurements of capacitance at the semiconductor-electrolyte interface. Anomalous changes in the space-charge capacity with applied potential have been attributed to the influence of deep-level electronic states, within or at the surface of the semiconductor. Surface states can limit the photopotential obtained in photoelectrochemical cells by "Fermi-level pinning" and can reduce the power efficiency by providing pathways for enhanced recombination. Although models for the semiconductor-electrolyte interface have traditionally been based on solid-state descriptions, the influence of ionic species, either through specific adsorption onto the surface or through adsorption in a diffuse double layer, needs further study. Even the applicability of traditional models for the diffuse double layer is questionable for the ionic concentrations typically used in photoelectrochemical processes. A better understanding of the electrolytic contribution to the semiconductor-electrolyte interface may be needed, for example, to explain the unexpectedly high photopotentials that have recently been reported.

- Homogeneous reactions in electrolytic solutions. Electrolyte modification has been pursued intensively as a means of providing high power efficiencies with low rates of photocorrosion by matching electrolyte and semiconductor properties. A very fundamental need exists for creating a thermodynamic data base for ionic species in a variety of solvents. The issues include the rate and equilibrium constants for electrochemically active species and the influence of electrochemically inert counterions (through adsorption or homogeneous interactions). Efforts in this area can also support the study of the kinetics and equilibrium constants for (heterogeneous) adsorption of ionic species, which can lead to shifts in the flat band potential.

- Microscale processes. The application of models to photoelectrochemical fabrication of submicron-scale structures requires consideration of different phenomena than are treated in models of larger scale systems. Surface roughening, tunneling, and double layer processes can play a major role on current (or reaction) distribution and selectivity; whereas, in contrast to large-scale systems, convective transport of electrolytic species may be comparatively unimportant. To be applicable, models must therefore account for the interactions between potential and concentration in the electrolyte close to the semiconductor surface as well as in solid-state processes.

The research areas listed above require that experimental studies be coupled with the parallel development and use of comprehensive mathematical models. Further development of photoelectrochemical energy conversion, fabrication of interfaces and structures, synthesis and detoxification, and characterization will be served with mathematical models that can be used to extract relevant physical properties, to guide experimental design, and to predict the response of the system based on well-founded hypotheses. Although the fundamental theory to be used is not new, the models must account for the complicated interactions among coupled physical phenomena. Interpretation based on simplistic models is often inadequate and can lead to misleading or incorrect conclusions.

VII. RESEARCH NEEDS AND OPPORTUNITIES IN PHOTOELECTROCHEMICAL SYSTEMS

Research in photoelectrochemical systems primarily aimed at energy conversion has achieved notable milestones and produced a variety of valuable spin-offs to other technologies and to the understanding of the underlying science. We conclude that the field deserves strong consideration for support within the broader context of photovoltaic systems. To accelerate this progress, a number of specific needs should be addressed, given in priority order:

1. Cross-fertilization between developments in photochemical and photovoltaic technologies.
2. Comprehensive studies of solution phase and surface chemistry and modification.
3. Increased level of characterization of the bulk, interfacial, and liquid phase properties of these systems, with stress on techniques capable of following the dynamics of the system.
4. Synergistic correlations of characterization and theoretical modeling.
5. Application of novel nanostructures that can amplify energy conversion schemes and other solar applications.
6. Development of more efficient and stable photoelectrodes to support substantive efforts for hydrogen production from solar energy.
7. Exploration of opportunities in electrochemical deposition and processing that can lead to very low-cost cells.
8. Integral storage schemes.
9. Fundamental understanding of etching processes and structurally sensitive control.
10. Development of photoelectrochemical strategies for enhancement of the environment (detoxification and synthesis).
11. Standardization of efficiency and stability measurements and testing procedures.

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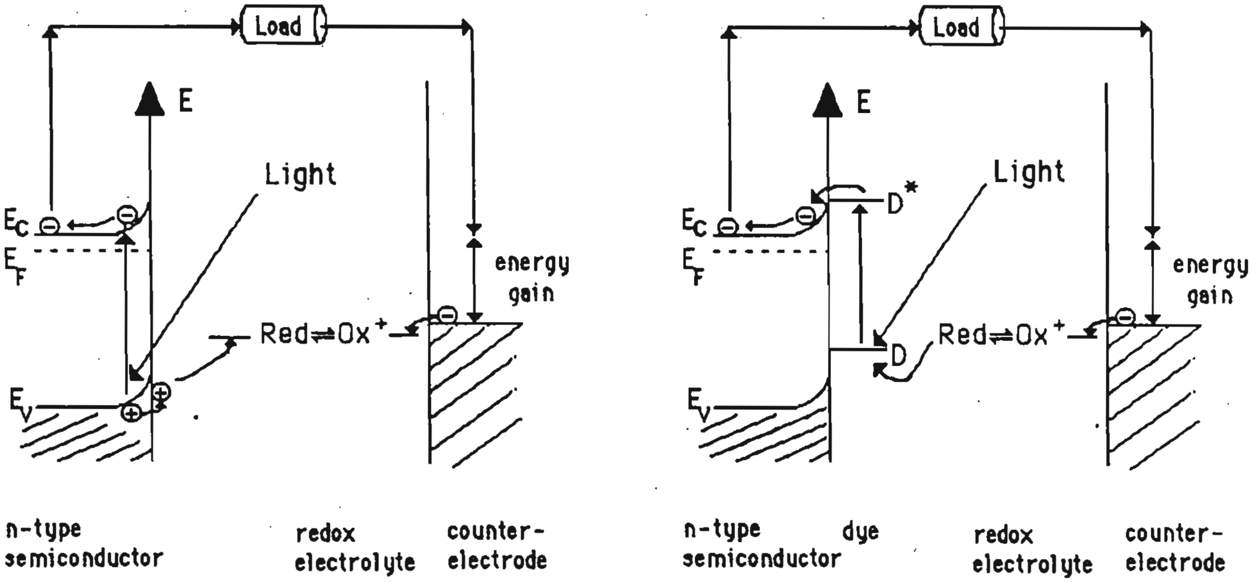

Figure 1. Carrier generation under illumination arising at (a) the semiconductor/electrolyte interface and (b) the semiconductor/dye sensitizer/liquid interfaces

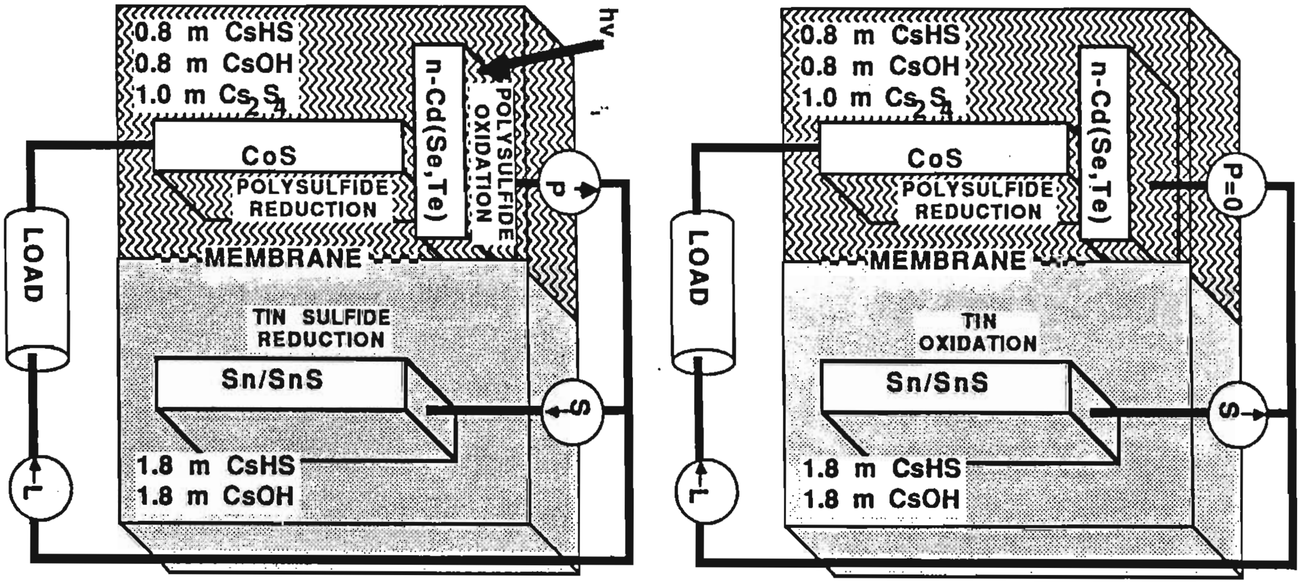

Figure 2. A PEC cell in a system combining both solar conversion and storage capabilities: (a) under illumination and (b) in darkness or low light

29. ORGANIZED MOLECULAR ASSEMBLIES

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SUMMARY

Organized molecular assemblies (OMAs)—self-assembled monolayers (SAMs), Langmuir-Blodgett (LB) films, vesicles, and lipid bilayers—represent a major, important new theme in condensed-matter science. SAMs, in particular, have properties suggesting potential wide applicability in control of interfacial properties for systems of interest to DOE. SAMs are systems at or close to thermodynamical minima, and are thus easy to prepare. The production of SAMs, unlike most surface technologies, is straightforward, and they are intrinsically manufacturable: they form highly ordered films by simple, low-cost processes, and they have low defect concentrations.

A. Characteristics of SAMs

We note these characteristics of SAMs as particularly relevant to the DOE mission:

- SAMs can be formed on rough, irregular, and shaped surfaces, as well as on inner surfaces and surfaces not accessible to line-of-sight methods.
- Damaged SAMs can be regenerated in situ, if the appropriate molecules are present in the immediate environment (i.e., as components in corrosion-, friction-, or soiling-control systems).
- The properties of SAMs can be varied with great flexibility, by control of their molecular components.
- Because the components of SAMs reliably form monolayers, small amounts of material will cover large surface areas: typically 1-10 kg of material might provide monolayer coverage of 1 km^2 of substrate. Processing with SAMs is thus intrinsically very economical and applicable to large-scale materials problems.

B. Recommendations for Research

1. Research in OMAs should focus on SAMs. Langmuir-Blodgett films have certain applications in multilayer systems and in research (for example, in optics), but the simplicity and economy of formation of SAMs and their applicability to rough, shaped, and interior surfaces make them much more promising for large-scale, cost-sensitive applications.
2. Support should be directed toward single-investigator projects. The style of research in SAMs focuses on small, individual research groups working alone and cooperatively. Instrumentation at the $100K to $1M level, which is often not shared, is an important component of this research. Large national facilities (light sources, etc.) are not crucial to the most important work in the field, although certain problems require access to these facilities. The national laboratories have not, so far, played a

significant role in the field, but might constitute a valuable resource at the technology-development stage.

3. The most important areas for basic research are:

- Development of methods for forming in-plane patterns and features in SAMs
- Use of SAMs for two-dimensional (2-D) organization of complex molecules
- Studies of SAMs as model systems for complex phenomena, including but not limited to: wetting, adhesion, friction, wear, interactions at biosurfaces, fouling, soiling, and corrosion
- Use of SAMs to study phenomena in condensed-matter science: cooperative behaviors, phase separations, and the influence of defects
- Use of SAMs to nucleate growth of condensed phases in three dimensions: condensation of water; growth of crystals; attachment of polymers
- Development of new types of SAMs, especially those with enhanced stability, and new types of surface-monolayer chemistry
- Development of computational models for SAMs and SAM-related phenomena.

4. The most important areas for generic, applied research are:

- Development of thermally and oxidatively stable SAMs formed from stable organic and inorganic components
- Direct application of SAMs to the most important classes of substrates—steels, aluminum, copper, semiconductors, ceramics, glass, and photolytically stable polymers.

5. Areas for applications research involving SAMs are:

- Corrosion Inhibition—Development of self-regenerating, passivating systems based on SAMs
- Tribology-Control Systems—Development of new, robust, self-regenerating systems for control of friction
- Soiling-Control Systems—Use of SAMs to develop easily cleaned surfaces (low surface free energy fluorocarbons; surface-attached hydrogels) for optical components and surfaces resistant to soiling and biofouling for membranes, and subsurface and marine structures
- Fuel Cells—controlling interfacial properties in gas/liquid/catalyst/membrane systems to improve performance.

SAMs are valuable in research as model systems for establishing the fundamental mechanisms of complex phenomena like corrosion, friction, wetting, wear, adhesion, biofouling, and surface charge dissipation. These studies will guide the design of coatings and thick films for practical applications for which SAMs are not sufficiently strong, stable, or robust. The most serious deficiency of SAMs in practical applications is their thermal, mechanical, and oxidative instability. Known systems are limited to temperatures below approximately 150°C, unless they can be used in self-regenerating form. The strategy of self-regeneration at a surface, accomplished in situ by including the molecular components of the SAM in the surrounding fluid or vapor, constitutes a unique and valuable characteristic of self-organizing systems.

LB films and other types of organized assemblies will also be useful, especially in research applications and in high-value uses such as optical and electrooptical devices.

I. INTRODUCTION: DEFINITIONS AND CHARACTERISTICS

Although the LB technique provided the first practical laboratory technique for constructing ordered molecular assemblies in the laboratory, this report focuses on self-assembled (SA) systems [1,2]. This focus by no means diminishes the importance of LB technology [3], but applications in the transportation and utilities technologies require emphasis on issues such as ease of film fabrication, stability, and cost—those that favor SAMs over LB films. This report deals with monolayers, though methods for fabrication of self-assembled multilayers based on molecular self-assembly have been developed in the last decade [4].

SAMs are OMAs that form spontaneously by adsorption of amphifunctional molecules at solid-liquid and solid-gas interfaces. These adsorbates have strong affinities—usually chemical in nature—to the substrate surfaces. The spontaneity of monolayer formation implies that such systems are thermodynamically stable. They are more stable than LB films, whose molecular components are often physisorbed to the surface of the substrate. That SAMs form in situ indicates that partially formed, disordered monolayers can be driven to complete, ordered systems, and that monolayers can self-regenerate in the presence of a molecular adsorbate.

There are many types of SAMs, including carboxylic acids on $A1_2O_3$, Ag_2O, and glass; phosphonic acids on di- and trivalent metal oxides; sulfonic acids on Ag_2O; disulfides and thioethers on gold; thiols on gold, silver, copper, and platinum; alkylsiloxanes on hydroxylated surfaces (Al_2O_3, SiO_2, glass, etc.); alcohols and amines on Pt. Common to the formation of all SAMs is an exothermic chemisorption step (e.g., ca. 40 kcal/mol for long-chain alkanethiols on gold) that provides most of the driving force for the process. The exothermicity of this chemisorption indicates that, unless there are interfering factors, these systems will maximize the number of adsorbed molecules on the surface, and generate a close-packed and ordered assembly. The other major contributions to order and stability in SAMs are interactions between the adsorbed chains (van der Waals, hydrogen bonding, etc.). The stabilization afforded by these interactions can be comparable in magnitude to the energies of chemisorption; for example, the van der Waals interactions for $C_{16}H_{33}S/Au(111)$ amount to approximately 26 kcal/mol.

The spontaneity of formation and high packing densities in these systems leads to films with few defects. This characteristic is very important when considering issues such as wetting, tribology, and electron transfer. The amphifunctional character of the molecules that form SAMs and the flexibility in molecular structure offered by organic synthesis provide the capability to tailor surfaces and to control their physical and chemical properties [5]. Incorporating functional groups into the alkyl chains of the adsorbates will allow the synthesis of increasingly more complex systems. Such studies are vital to both detailed understanding of self-organization and to the development of advanced materials and their applications in technology.

To summarize, the properties of SAMs most important in technology relevant to transportation, utilities, and conservation are:

- Spontaneity of in situ formation
- Thermodynamic stability
- Ability to apply conformal coatings on surfaces, regardless of their shape
- High packing densities and low defect concentrations
- Molecular alignment
- Capability to tailor surfaces to desired applications
- Synthetic flexibility.

II. SCIENTIFIC OPPORTUNITIES

Unique opportunities for increasing our understanding of thin-film structures, surfaces, and interfaces involving molecular materials are available to researchers who use SAMs. These fundamental studies will have broad importance in the areas of materials science, condensed matter physics, chemistry, and the biological sciences. They will have broad relevance to generic problems in surface and interface modification, and to certain classes of problems in manufacturing and energy conservation and generation.

A. Condensed Matter Science

Recent applications of SAMs to the physics of 2-D condensed matter are particularly interesting. SAMs provide the opportunity to study the effects of dimensionality in phase transitions and the correlations between phase states, structural coherence, and molecular size and shape. The highly controlled surface structure in SAMs also provides opportunities for new experimental approaches to understanding the difficult problem of nucleation and growth of molecular crystals. In this context, biomimetic nucleation of crystal growth represents a growing area of research relating to SAMs that offers exciting opportunities for fundamental study in materials science [6]. The organization of crystalline materials on modified surfaces should not be limited to inorganic salts, but should be viewed as a more fundamental phenomenon. Nonetheless, establishing the rules governing biomineralization may provide inexpensive routes for the production of ceramic materials that are of interest to DOE.

B. Heteroepitaxy

One of the premier issues in materials science today is the question of how to accomplish heteroepitaxy: that is, how to fabricate the most defect-free interface between a crystalline substrate and a deposited, crystalline overlayer of another material with different lattice constants. A well-known, purely inorganic example is the continuing effort to grow GaAs on silicon by molecular beam epitaxy. Creative uses of SAMs, with appropriate chemical and thermal stability, as templates to assist such heteroepitaxy by fine-tuning changes in lattice spacing over molecular distances, would be of great interest.

C. Nanostructures

Another area of great importance at the intersection of materials science and physics is the fabrication and electronic properties of surface structures patterned at the nanometer scale [7]. High-resolution, lithographic processing demands the use of resist films with nanometer-scale thicknesses and low defect concentrations. The combination of high chemical flexibility and other suitable properties makes SAMs an attractive possibility [8]. The ability to create structures such as nanowires and quantum dots has been a key factor in the development of the physics of quantum confined structures. Another intriguing possibility in materials science is that of using SAMs for information storage applications. One approach is suggested by the work of Fujishima and coworkers [9]. This group used the optically induced isomerization to modify the redox potential of surface-confined species in an LB film. The resulting heterogeneities in the film could be read by simple electrochemical methods.

There are several major opportunities to use SAMs to help resolve long-standing scientific issues in the chemical sciences. The high flexibility to synthesize surfaces with well-defined arrays of functional groups should continue to provide major advances in the understanding of wetting and surface chemical phenomena. This research will provide new understanding of the complex interfacial behavior that underlies the performance of a range of natural and synthetic structures, including environmentally protective coatings, biocompatible surfaces, highly specific biological receptor sites, and advanced composite materials. Studies of the organization of complex molecules, polymers, oligopeptides, and other biomolecules are important to derive an understanding of the relation between the structure of an individual molecule and its organization in two dimensions. Such fundamental understanding is vital for the advancement of materials science.

III. OPPORTUNITIES FOR APPLICATIONS IN TECHNOLOGY

Beyond the fundamental studies, there are now a number of problems in technology to which SAMs and other OMAs can be applied [10]. The following list is incomplete, but it provides examples that illustrate the types of problems for which SAMs may provide solutions.

A. Fuel Cells

A broad range of problems in the technology of phosphoric acid-organic membrane fuel cells centers on the control of interfaces, and SAMs may be useful in solving a number of these problems. Among the potential applications are:

- Controlling the wettability of pores in the gas distribution membranes to facilitate the transport of gases to the cathode and anode surfaces, to control the wetting of these and surrounding surfaces, and to control the removal of water from the cathode
- Controlling the interface between the platinum and the carbon support to limit corrosion
- Controlling the interface between the carbon and the ionomer surface layer to ensure good proton conductivity
- Improving adhesion between the catalyst-containing surface ionomer layers and the central ionomer membrane
- SAM-forming additives may, speculatively, be useful in controlling the kinetics of redox processes at the interfaces. An oxygen reduction catalyst that would adsorb at the cathode surface and increase the rate of reduction of 0_2 to water would lead to large improvements in cell performance. By using a self-regenerating layer, it would be possible to compensate for material lost by corrosion or electrochemical damage.

B. Photoelectrochemistry

Monolayer films offer interesting opportunities in electrode modification. The simplest, yet most important application, is electrode passivation, especially for materials like amorphous silicon, that are unstable in aqueous media. Using simple n-alkyl derivatives as adsorbates for passivation introduces an insulating layer at the electrode, thus decreasing electron transfer and cell performance. Using more conductive derivatives, however, would overcome this problem. New possibilities have been reported recently for the stabilization of semiconductor interfaces [11]. SAMs have been demonstrated to provide useful protection of metal (Cu, Au) surfaces against chemical corrosion. Adsorption of a SAM on a photoelectrode may also help to passivate surface states and thus reduce losses in efficiency due to electron-hole recombination, without inhibiting electron tunneling across the interface.

Synthetic models for photosynthesis may be important for engineering specific photoelectrodes. Modifying these electrodes with appropriate monolayers would result in a modified potential that can carry out a specific, clean chemical reaction. Advances in photoelectrochemical catalysis may also result from research on SAMs, although it would likely require the use of organometallic derivatives.

C. Thin Film, Multilayer, Solar Collectors

OMAs should be useful in addressing those problems with photovoltaic (PV) panels and concentrators, solar collectors, and electrochromic (EC) windows that require tuning of surface properties. Current spending for research on PV modules is about $40M/year, with only $600K set aside for encapsulation studies. PV efficiencies have reached more than 17%, and operation at this efficiency for 30 years would make these modules economically viable.

The lifetime of PV modules is currently limited by the photothermal degradation of the polyethylene vinyl acetate (EVA) copolymer presently used as a protective coating. This photodegradation causes the film to darken and leads to losses of 5% to 15% (or more in some cases) during 5 to 10 years of operation in hot, dry climates. This process proceeds most rapidly from the interface between EVA and the soda lime glass superstrate, as well as from around the "fingers" of metallization that protrude into the film. Replacement of EVA is now being considered, but similar photodegradation problems will likely be encountered with other polymeric layers, especially at the metal (oxide)/polymer interfaces. The photochemical stability of these sensitive interfaces may be significantly enhanced by SAMs used as low-dielectric coatings that also serve as diffusion barriers between different layers.

The efficiencies of flat-panel PV arrays, PV concentrators, and the heliostats of mirror fields are reduced by repetitive cycling (through soiling and cleaning) that accompanies environmental exposure. Exploratory work indicates that soil retention can be mitigated, and possibly eliminated, by treating the outer surfaces with a single oriented layer of a fluorinated amphiphile (see Chapter 18 in this volume). Samples treated in this way retain their original reflectances for more than a year and through 20 soiling/cleaning cycles. Longer-term studies are required to determine specific lifetimes.

EC windows have a minimum of five layers of active materials and eight interfaces, including poorly understood interfaces between ion-storage and ion-conducting layers as well as interfaces from a superstrate and substrate. The barrier and dielectric properties of SAMs at these interfaces might play an important role in maintaining layer segregation and operating efficiencies. Antisoiling SAMs at the outer surfaces may also be beneficial.

D. Polymer/Metal (Oxide) Interfaces

SAMs offer potentially significant benefits in systems that require strong bonding between a metal (oxide) substrate and a polymer. These systems include conformal coatings of protective films, adhesives, primers, and paints. As mentioned in the opening section of this chapter, the formation of SAMs is driven by strong chemical bonding of the adsorbates to the substrate. Adsorbates may be modified by organic synthesis, before or after adsorption, to incorporate reactive end-groups that can be used to covalently attach a polymeric coating to the surface. The high packing densities, low defect concentrations, and molecular alignment of these films should provide efficient multisite linkages between the substrate and polymer [12].

This technology may also offer advantages in reducing the number and/or complexity of required processing steps for fabricating metal (oxide)/polymer materials. As an example, a critical concern in forming a strong adhesive bond is the cleanliness of the substrate. In a typical preparation of a SAM, however, the desired adsorbate displaces physisorbed organic contamination, and the monolayer film is usually less prone to contamination than the bare metal (oxide). Hence the process is, in some circumstances, self-cleaning and self-passivating. As the number of systems known to form SAMs grows, the need for some processing steps (e.g., removing the native oxide from the substrate) may also become unnecessary. Elimination of processing steps is advantageous economically and in terms of environmental impact.

IV. TECHNOLOGICAL PROBLEMS: LIMITATIONS TO THE TRANSFER OF SCIENCE INTO TECHNOLOGY

Basic research has established a range of properties for the most useful OMAs—SAMs formed by spontaneous chemisorption of organic molecules onto surfaces—that make them potential solutions to a broad range of technological problems of concern to DOE. The most relevant of these properties involve the ease and economy with which SAMs can be formed, and the flexibility with which their properties can be tailored by controlling the structures of the component molecules through synthesis. Because these systems are at thermodynamic minima, they are intrinsically defect-free and self-healing. SAMs form with high degrees of order on exposure of the surface to the adsorbing species; the technologist does not have to stabilize a metastable system. Clean-room conditions are not needed in SAMs preparation; their enthalpy of formation is often enough to clean the substrate surfaces by displacing dust and weakly adsorbed contaminants. SAMs will cover defects and can be formed on irregular and interior surfaces.

The major limitations to the application of SAMs in many technologies are their limited thermal, photochemical, and oxidative stability; an incomplete base of knowledge to guide their formation on many classes of substrates; and their low mechanical strength. Each of these limitations can be circumvented or minimized by developments of existing science, or by extension of already demonstrated paradigms to new classes of materials.

A. Stability

Most work with SAMs has focused on components derived from polymethylene-based organic molecules $X\text{-}(CH_2)_n\text{-}Y$, in which the X group forms a bond with the surface and the Y group provides the function or tailors the interfacial properties. The polymethylene chain is subject to thermal damage; the chain oxidizes relatively readily in contact with air at temperatures greater than 100°C. For many applications, higher stability is required.

The obvious approach to this problem is to develop SAMs based on polymeric models of known stability. For example, components for SAMs may be based on polyarylsulfones and -ethers, polyimides, poly(diorganosiloxanes), fluorocarbons, polyphosphazines, and a range of other polymer structures that are already used for applications that require stability under extreme conditions. These systems could be modified for use in SAMs, either as functionalized oligomers or as functionalized polymers [13]. SAMs prepared from these structures can be confidently predicted to show much greater thermal and oxidative stability than those now known. It is probable that appropriate representatives of these systems will be usable in applications requiring exposure to air at temperatures of approximately 300°-400°C for short times. For higher-temperature applications, it will be necessary to make a greater step in technology. In principle, it should be possible to build SAMs of inorganic components with very high stability (carboranes, metal oxide clusters), but these types of systems have not yet been explored.

B. Monolayer-Substrate Interactions

Much of the research on SAMs to date has focused on well-defined, convenient model substrates: gold and silver, alumina, silica, and mica. Other metals and metal oxides have been surveyed casually, and there is every reason to expect that SAMs with high order can be formed on a range of substrates, but the appropriate surface chemistry for forming SAMs on "real" materials—native oxides on steel, aluminum alloys, copper, bronze and amorphous silicon, multicomponent silicate glasses, silicate minerals, concrete and others—have not yet been developed. A program to develop the surface coordination chemistry appropriate for these substrates will be essential. The broad principles to be followed are well-known, but the practical details remain to be established.

C. Mechanical Stability

SAMs typically have thicknesses of the order of 1 to 5 nm. They will not be mechanically strong. Even if they were, the underlying substrates would fail under the same mechanical stresses as they would if unprotected. The appropriate strategy for using SAMs to protect against mechanical wear will be to take advantage of their capability for in situ repair. Thus, for example, for a SAM to be useful in the control of friction or corrosion in an application in which mechanical damage or wear is probable, the wear surface should be exposed to a solution or vapor of the molecules making up the SAM. Wear will occur, but the SAM will regenerate itself in situ. For a solution to be used in cleaning exposed surfaces of PV systems, the components of a surface-protective SAM can be included in the cleaning solution. This capability for in situ regeneration is well-established in model systems and is the basis for the use of fatty acids and derivatives as additives for control of corrosion, wetting, and friction. These types of self-healing processes must, however, be studied in greater detail to provide a science and engineering base appropriate for design in new applications.

D. Other Applications

There are many other potential applications of SAMs in the development of new technologies. For example, SAMs could be used as "masks" to control deposition of metal oxides or metals in new types of coating or electrodeposition processes. Existing systems are already excellent wetting and adhesion promoters, but have not been developed for processes involving painting, or adhesion and wetting in manufacturing applications.

E. Recommendations

The highest-priority generic opportunities for moving SAMs into technology are:

- To develop SAMs with high thermal and oxidative stability
- To develop the surface chemistry necessary to form SAMs on important classes of materials (steels, metal oxides, semiconductors, other metals, and ceramics)
- To develop and demonstrate strategies for regenerating SAMs in situ, especially under conditions in which wear or mechanical damage may be important.

V. NEEDS IN RESEARCH

A. Overview

Multidisciplinary approaches to research and research instrumentation are two issues that must be properly addressed and resolved in order to ensure rapid and efficient progress in capitalizing on the scientific opportunities and solving the technological problems mentioned above.

At this stage of development in the field of SAMs, the problems are primarily those of the chemical sciences. In parallel with the typical structure of an inorganic substrate and a chemically bonded organic overlayer, a typical research group poised for the fastest advancements in the field might be one combining the skills of traditional disciplines of inorganic, organometallic, and organic chemistry. Such a combination will ensure capability in broad, creative approaches to building unprecedented, mixed inorganic/organic materials that have potential relevance to technological problems. Beyond the synthetic aspects, however, equal efforts are needed from analytical and physical chemists to provide quantitative analyses of the new structures and a detailed understanding of the formation mechanisms that lead to desired properties. The utility of the SAM will depend on some critical property. In many cases, these properties may be relatively complex such as an optoelectronic or biological response, or an influence on corrosion or wear. The cooperation of other experts such as materials scientists, physicists, electrical and mechanical engineers, or biologists would be of obvious help. Although there is no question that critical advances in this technology can be made by individual specialists, we highly recommend that multidisciplinary efforts be encouraged to provide novel and creative approaches.

There are clear instrumentation needs to support the tasks of quantitative chemical and structural analysis of these organized structures. The combination of subtle but critical structural features, sensitivity towards degradation, and the monolayer-level amounts of materials has resulted in the emergence of only a few dependable instrumental techniques for analysis in these systems (see characterization section). There is a need for further development of instrumentation to solve these difficult, nontraditional analytical problems, and such efforts should be encouraged. For existing instrumentation, there are two categories of issues: those dealing with independent investigator instrumentation and those dealing with multiuser facilities. The majority of analytical efforts will require laboratory-centered instrumentation, such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIRS), and secondary ion mass spectrometry (SIMS). It is clear that the most advanced and meaningful studies of SAMs will require the use of this type of instrumentation on a regular basis. Some of the more recent and detailed analyses now include the use of national facilities, in particular synchrotron sources for in-plane X-ray diffraction and near-edge X-ray fine structure spectroscopy. As the field moves to problems requiring imaging analysis, scanning Auger and static SIMS will become more important. Scanning tunneling microscopy (STM), atomic force microscopy (AFM), and related techniques such as near-field imaging are also increasingly valuable in characterizing local structure down to the atomic level. Brewster angle microscopy and high-sensitivity scanning electron microscopy (SEM) are becoming important techniques. Although only limited use of such facilities is needed, it is very important that these facilities continue to be readily available to users working on the chemistry of organic films. The lack of additional facilities of this type, however, is not limiting the progress of research at this time.

B. Payoffs

Support of fundamental and applied research into SAMs will lead to energy savings through enhanced understanding of interfacial processes vital to almost every technology. These technologies include:

1. Tribology

SAMs are already known to confer new friction and wear characteristics on substrates, in all cases improving wear resistance. Because the effects of SAMs on boundary-layer lubrication can be modeled computationally, such studies will enhance mechanistic studies and provide a basis for practical improvements.

2. Fuel Cells

SAMs can provide technology for surface modification that will improve the manufacturability and operation of fuel cells in several areas: improved adhesion and contacts between components with fewer defects and leaks; improved capability to control gas distribution to the electrode surfaces and water distribution at (or removal from) these surfaces; possibly improved overall performance of the cells as redox catalysts for the cathode, thus dramatically affecting energy costs.

3. PV Cells and EC Windows

SAMs may find applications as protective coatings or adhesion-promoting layers for both active and passive components of PV cells and EC windows. Chemisorbed monolayers having close-packed alkyl chains should decrease diffusion rates of water to, and their condensation at, interfaces containing polycrystalline active layers (e.g., CdTe), processes that are probably associated with failure of almost all devices. These monolayer films might also increase device lifetimes by stabilizing heterojunctions (e.g., CdTe [p]/CdS [n]) or "fingers" of metallization. One of the most immediate benefits in this area may be in relating modes of failure at critical device interfaces to their molecular and atomic compositions. The potential applications of SAMs for the encapsulation of passive components, such as mirrors and solar collectors, are discussed in the following section.

4. Surface Contamination: Soiling and Fouling

Interfacial contaminants can interfere with virtually every industrial unit process, thereby increasing energy consumption, even if their concentration in the bulk is very low. Systematic modification of surface properties—critical surface tension, hydrogen-bonding capacity, polarity, dispersion-force energies, and extent of fluorination—using SAMs will clarify the mechanisms by which industrial streams contaminate equipment, thereby facilitating prevention. Heat-transfer pipes are notoriously subject to fouling and clogging, and should be given top priority for antisoiling treatment with SAMs designed for high-temperature stability.

5. Fouling in Membrane Separations

Distillation, an enormously energy-consumptive technology, still accounts for 95% of U.S. industrial separations. Almost all of these separations could be carried out more efficiently, near ambient temperature and with much less waste of products, using membrane technology (microfiltration, ultrafiltration, reverse osmosis, electrodialysis, etc.) or hybrids of membrane separations with other methods. Membrane fouling, which reduces efficiency and raises costs, has strongly inhibited substitution of membrane separations for distillation. Fluorinated LB monolayers can, in certain circumstances, virtually eliminate membrane fouling, and fluorinated SA monolayers should confer the same benefit. Further research and development and lifetime-testing are essential.

The National Research Council reported in 1983 that a critical need for improved detection by sensors is improved membranes for selective transport between source and sensor. A nonfouling membrane is also necessary for this application in any real environment.

6. Selectivity in Membrane Separations

The polymeric and ceramic membranes now commercially available each have wide ranges of both pore size and selectivity. Selectivity in these systems depends on the pore diameters and the physicochemical interactions between the membrane and feed stream. The only exceptions to the problem of nonuniform pore size are "drilled" polycarbonate membranes, which have regular pores with nearly zero taper, but these membranes are inapplicable for many separations because of their large pore diameters. SAMs provide the means for healing the surface defects that account for much nonselective flux through standard membranes, adjusting pore sizes by deposition of films within pores, modifying the surface wettability of membranes to optimize separations, and adjusting the surface chemistry of membranes to optimize interactions with given feed streams.

Membranes with optimized selectivity are needed to provide chemically selective sensors and detectors. A related application of membranes anisotropically treated with SAMs is done in protective suits that do not allow diffusion of pesticides, pollutants, and chemical-warfare agents, while allowing the diffusion of moisture and CO_2, and the conduction of heat. This type of selectivity has been demonstrated, in fact, using LB films.

7. Biosurfaces

Natural cell membranes are OMAs with a minimal tendency to agglomerate proteins or cause other deleterious physiological reactions. Synthetic OMAs (e.g., those comprising organized phospholipids or derivatives thereof) have the potential for mimicking the characteristics of natural cells for in vivo applications without introducing materials that would be recognized as foreign. SAMs composed of these materials, therefore, offer great potential for coating prosthetic devices and implants, as well as for optimizing the biocompatability of hemodialysis membranes and the surfaces in devices such as heart-lung machines [14,15].

Biofouling is an important problem in a very broad range of technologies—marine corrosion due to anaerobic archaebacteria, corrosion of buried power cables, contamination of heat-transfer surfaces in cooling towers causing a decrease in thermal efficiency, and decreased efficiency in ship transportation due to marine growth on hulls. SA organic structures will certainly be the best systems with which to determine the fundamental molecular processes underlying these types of fouling, and the results will aid in the design of improved systems (for example, engineered polymer coatings) for their control. In certain circumstances, SAMs themselves may be solutions to the problems. For examples, appropriate additives in cooling towers or heat exchangers may provide optimal strategies for controlling biofouling in these systems. Inclusion of SAM-forming components in polymers, in a way that would permit them to "bloom" to the surface, might be effective in preventing microbial adhesion and formation of slime layers.

8. Sensors

SAMs, by virtue of the flexibility with which they can be modified, provide the basis for technology that will introduce sensor molecules into appropriate systems [16]. For example, SAMs have already been built into small-area (ca. 1 μm^2) sensors for pH and ion-concentration measurement [17,18]. SAMs involving immobilized antibodies are the basis of a highly promising new technology using surface plasmon spectroscopy to carry out biospecific detection [19,20]. The recently developed method for attaching SAMs directly to the bare surface of GaAs suggests possibilities for developing new classes of chemical-sensing, semiconductor devices [11]. For a range of sophisticated environmental sensors of interest to DOE, SAMs will probably provide the best technology for introducing molecular recognition capability in optical and electrochemical systems.

9. Corrosion

Corrosion inhibition is an area in which SAMs have traditionally played an important role, although it has not always been recognized as such. Long alkyl chains, for example, form excellent barriers to H_2O, O_2, and various other corrosive agents. A better understanding of the principles underlying this phenomenon should lead to the rational design of SAMs for applications in corrosion inhibition involving a wide variety of both metals and semiconductors. SAMs could also be useful in coupling chemically labile substrates (e.g., copper) and chemically resistant layers (e.g., a micron layer of polymer), a strategy that would increase the mechanical durability of the interface.

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A1. OFFICE OF BASIC ENERGY SCIENCES (OBES)

The OBES supports basic research under the following divisions:

Materials Sciences
Chemical Sciences
Energy Biosciences
Engineering Geosciences
Advanced Energy Projects

DIVISION OF MATERIALS SCIENCES (DMS)

The DMS supports basic research on materials properties and phenomena important to all energy systems. This research is performed primarily at the DOE national laboratories and universities. The research covers a spectrum of scientific and engineering areas of interest to DOE. The aim is to provide the necessary base of materials knowledge required to advance the nation's energy programs. For more information about the research sponsored by the DMS, the publication entitled "Materials Sciences Programs" is available in limited quantities by calling the DMS at (301) 903-3426 [1].

The DMS also supports a number of National User Facilities that are mainly used for the characterization of materials and research involving the interaction of photons, neutrons, or ions with materials. For more information, the publication entitled "Scientific User Facilities, a National Resource" is available in limited quantities by calling the DMS at (301) 903-3426.

The total operating budget of the DMS in FY 1989 of $180M was divided by discipline as follows:

Metallurgy, Materials Science, Ceramics	30.6%
Physics, Solid State Sciences, Solid State Physics	28.1%
Materials Chemistry	10.3%
Facility Operations	31.0%

The DMS supports a variety of research topics that provide the basis for "surface processing."

The following summary (for FY 1989) gives the number of projects supported by the DMS that use the listed techniques and may be used for characterization of surfaces:

Auger Electron Spectroscopy	46
Electron Diffraction Technique Development	28
Electron Energy Loss Spectroscopy	30
Electron Spectroscopy for Chemical Analysis	15
Ion Channeling of Scattering	18
Infrared Spectroscopy	23
Laser Spectroscopy	31
Raman Spectroscopy	23

The following summary (for FY 1989) gives the number of projects supported by the DMS that use the listed method and may be used for surface modification:

Chemical Vapor Deposition	22
Surface Treatment and Modification	47
Ion implantation	
Laser processing	
Electron beam processing	
Sputtering	
Coatings	20

The following summary (for FY 1989) gives the number of projects supported by the DMS that specifically study surfaces:

Chemisorption	39
Physisorption	21
Structure	47
Thin Films	61

Abstracts of program summaries that are most relevant to surface processing and compiled in Reference 1 are:

1, 31, 33, 40, 42, 48, 49, 58, 69, 70, 84, 92, 99, 101, 102, 105, 112, 113, 118, 120, 132, 134, 149, 155, 163, 168, 171, 180, 187, 190, 192, 200, 206, 209, 220, 221, 222, 226, 231, 250, 267, 271, 286, 333, 346, 349, 351, 366, 397, 404, 417, and 425.

The DMS supports the following user facilities that are likely to be useful in the study of surfaces:

National Synchrotron Light Source
Brookhaven National Laboratory

Stanford Synchrotron Radiation Laboratory
Stanford University

Electron Microscopy Center for Materials Research
Argonne National Laboratory

Shared Research Equipment Program (SHaRE)
Oak Ridge National Laboratory

Center for Microanalysis of Materials
University of Illinois

Surface Modification and Characterization Collaborative Research Center
Oak Ridge National Laboratory

Combustion Research Facility—Materials Program
Sandia National Laboratories

National Center for Electron Microscopy
Lawrence Berkeley Laboratory

The DMS has supported the following workshops that may contain information useful for "surface processing":

"Research Opportunities on Cluster and Cluster-Assembled Materials—A Department of Energy, Council on Materials Science Panel Report," R.W. Siegal, L.E. Burns, et al., J. Mater. Res., 4(3), 704 (1989).

"Fundamental Issues in Heteroepitaxy—A Department of Energy, Council on Materials Science Panel Report," P.S. Peercy, et al., J. Mater. Res., 5(4), 852 (1990).

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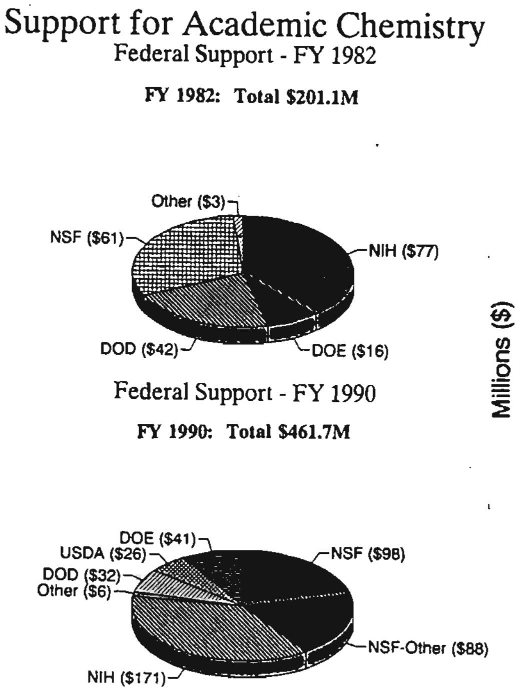
A2. NATIONAL SCIENCE FOUNDATION (NSF)

The summary of surface processing relevant research supported by the National Science Foundation has been prepared by Peter Sherwood, Department of Chemistry, Kansas State University, Manhattan, KS 66506, who served as Program Officer for Analytical and Surface Chemistry from September 1990 until September 1991. The summary thus represents his personal reflections of the situation at that time.

SUMMARY

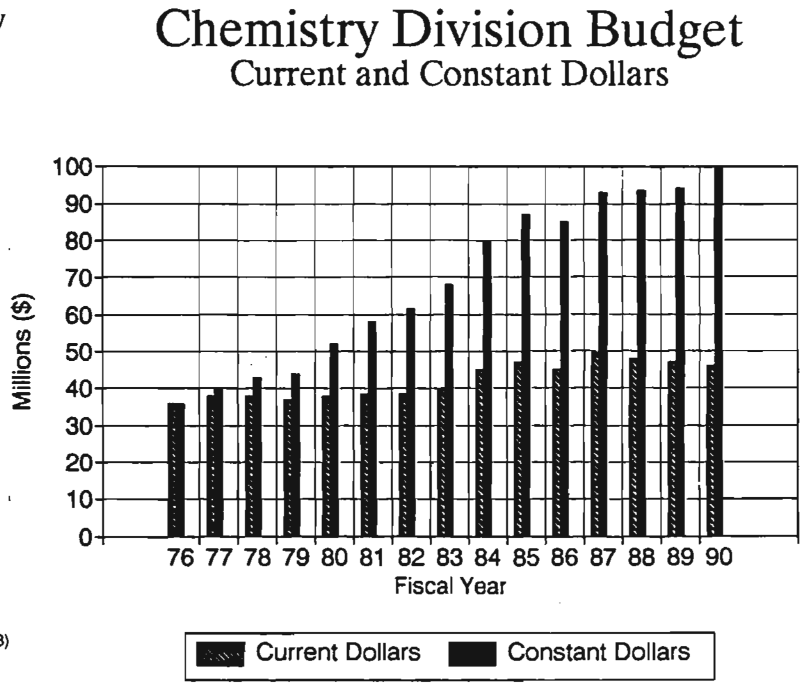
Surface Science is funded by a number of divisions of the National Science Foundation (NSF). The main support is provided by the Chemistry Division, the Division of Materials Research, and Chemical and Thermal Systems. In the Chemistry Division, the support comes largely from the Analytical and Surface Chemistry Program. In the Division of Materials Research, the support comes largely from the Solid State Chemistry Program and the Electronic Materials Program.

The charts that follow refer to the Chemistry Division Program.



Support for Academic Chemistry
Federal Support - FY 1982
FY 1982: Total $201.1M

Federal Support - FY 1990
FY 1990: Total $461.7M



Chemistry Division Budget
Current and Constant Dollars

Chart 1: The changes in support for academic chemistry from FY 1982 to FY 1990.

Chart 2: Changes in the Chemistry Division budget over the years. Note that the budget is approximately the same in constant dollars, but the number of research active university faculty has increased considerably.

CHEMISTRY DIVISION - KEY STATISTICS

- **900 Research Grants in 1990**
- **81% of CHE funds go to individual investigators**
- **33% success rate for research grants**
  (higher for renewals, lower for first applications)
- **17% of budget spent on instrumentation**
  - **$7.6 million - departmental**
  - **$9.7 million - individual**
- **Presidential Young Investigator Awards - up to 20 per year**
  ($100,000 5-year grants with industrial matching funds)
- **Postdoctoral Fellowships - 15-20 per year**
  ($26,000 stipend, 2-year tenure, starter grant option)

Chart 3: The activities of the Chemistry Division in FY 1990.

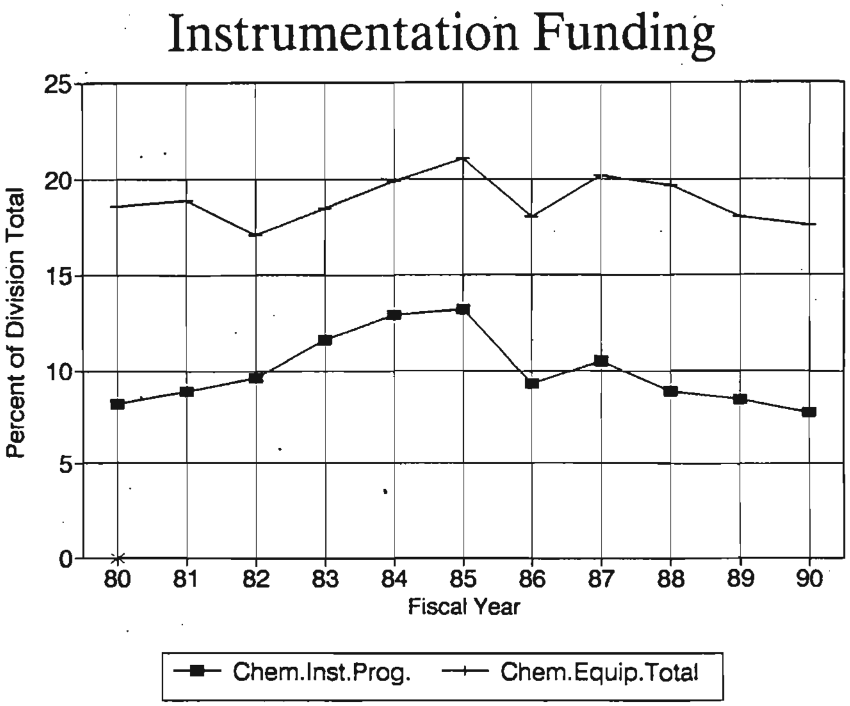
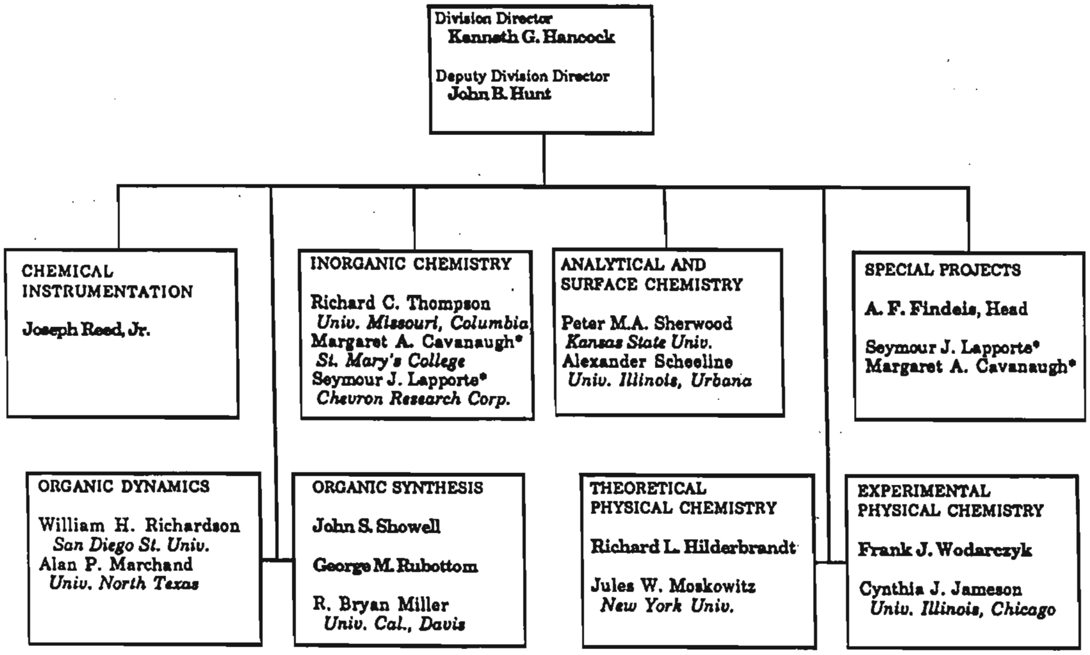


Chart 4: Distribution of funding for equipment between the Chemical Instrumentation Program (CIP) and normal research grants. The CIP requires matching monies and multiinvestigator proposals.



[1] Permanent staff listed in boldface

*Indicates half-time responsibility

Chart 5: The programs comprising the Chemistry Division in FY 1991.

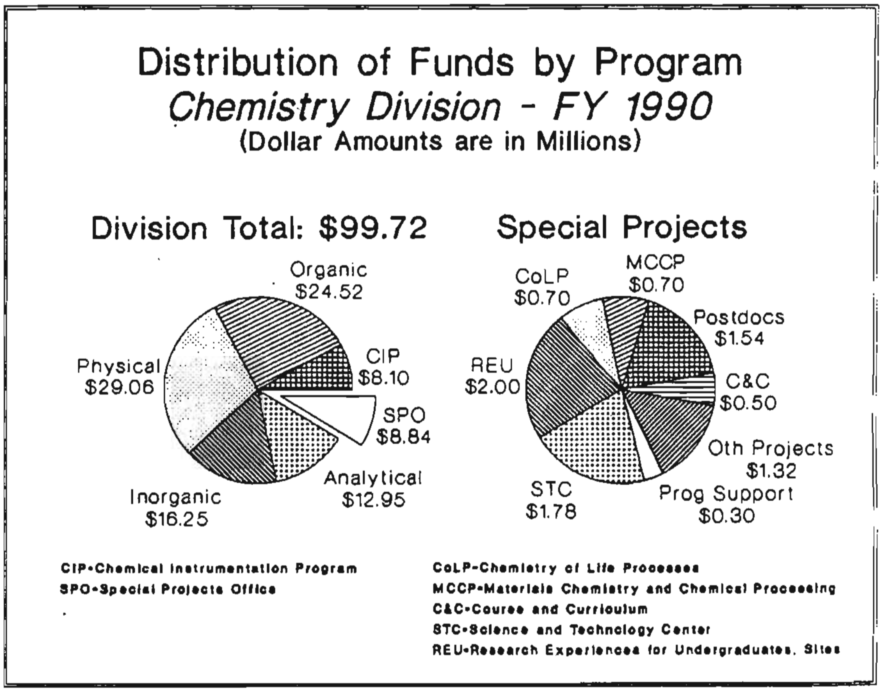


Chart 6: The distribution of funds among the Chemistry Division programs in FY 1990.

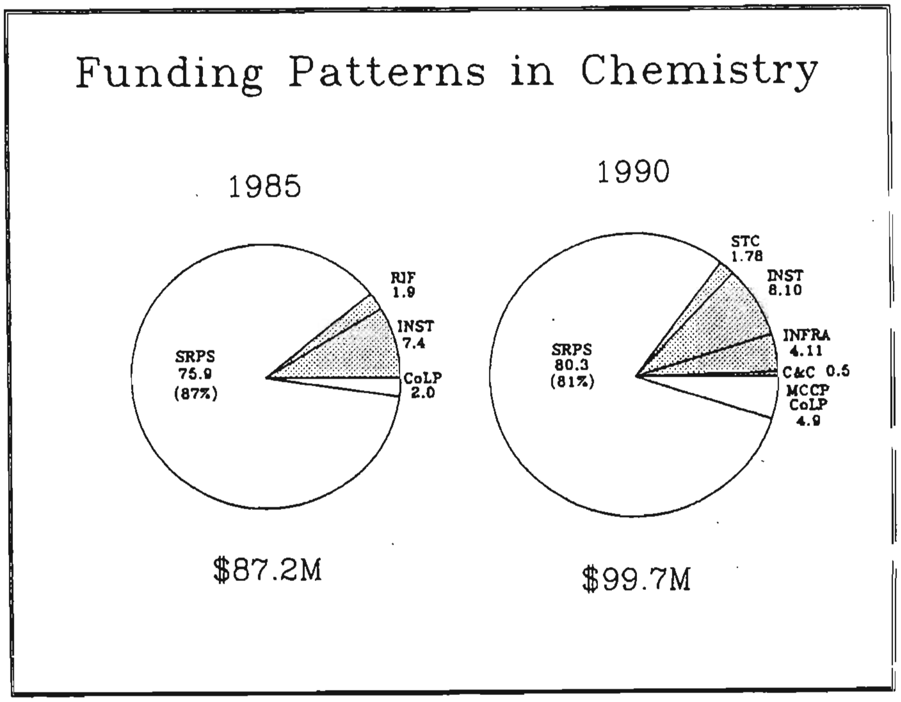


Chart 7: The change in distribution of funds to normal research grants (SRPS) and special research programs between FY 1985 and FY 1990, in which STC denotes the science and technology centers, INST denotes the chemical instrumentation program, INFRA denotes the infrastructure support, MCCP denotes materials chemistry and chemical processing, and COLP denotes the chemistry of life processes.

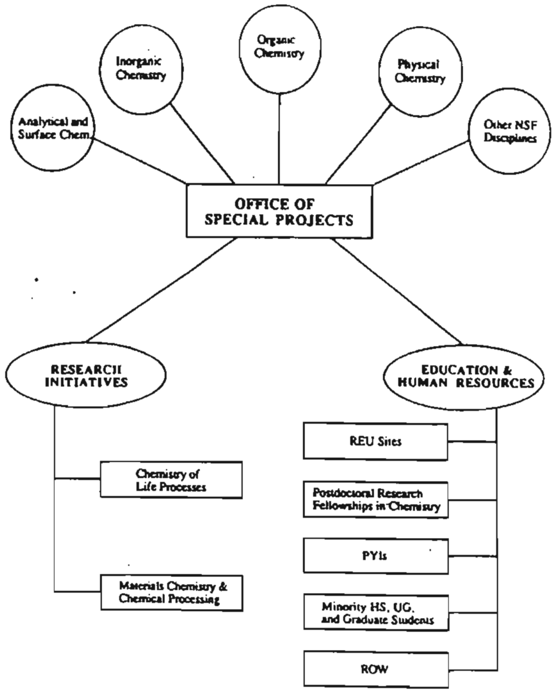


Chart 8: Activities of the Office of Special Projects.

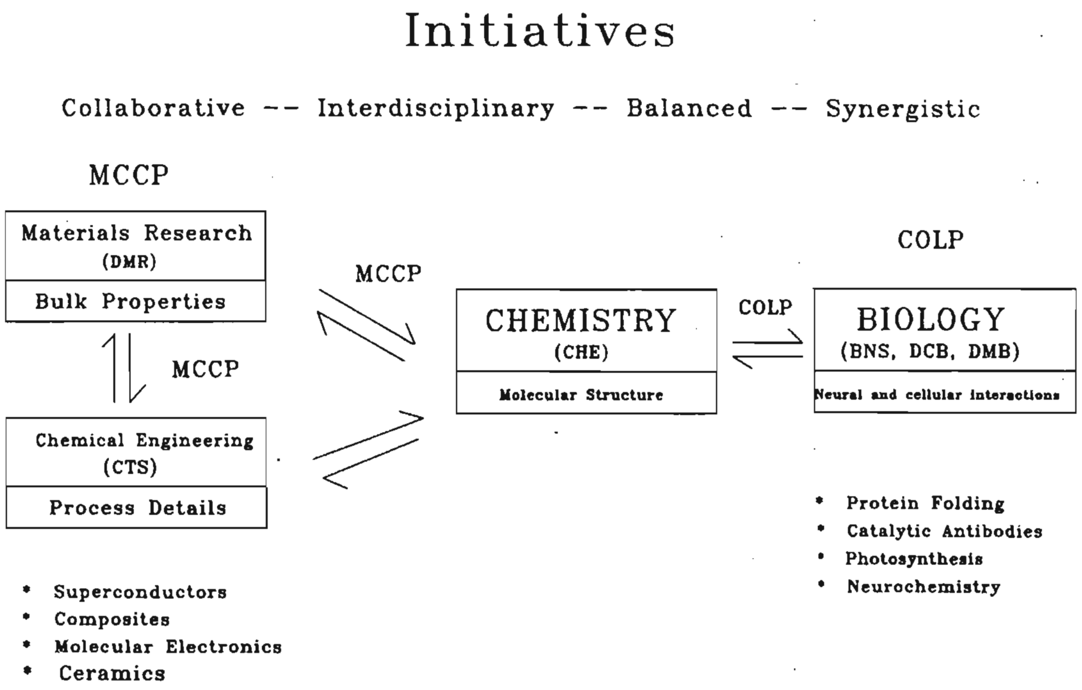
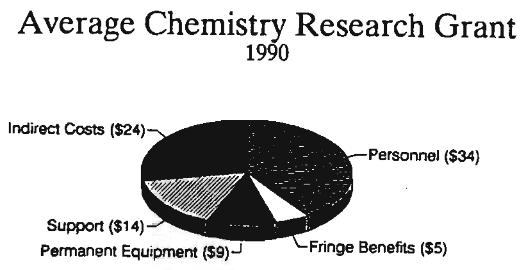
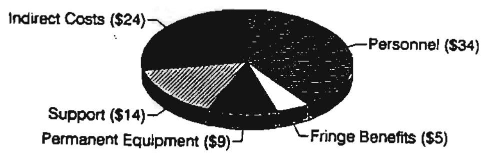


Chart 9: The MCCP and COLP Initiatives in FY 1990. (Please note that MCCP has been replaced by the Materials Synthesis and Processing Initiative involving nine NSF divisions in FY 1992.)



Average grant budget in thousands of dollars



Salaries, wages, and fringe benefits ($38.8 thousand) for the average grant

Average grant size is $85,500 per year: Range is $30,000 to $300,00 per year

Chart 10: The Average Chemistry Research Grant in FY 1990.

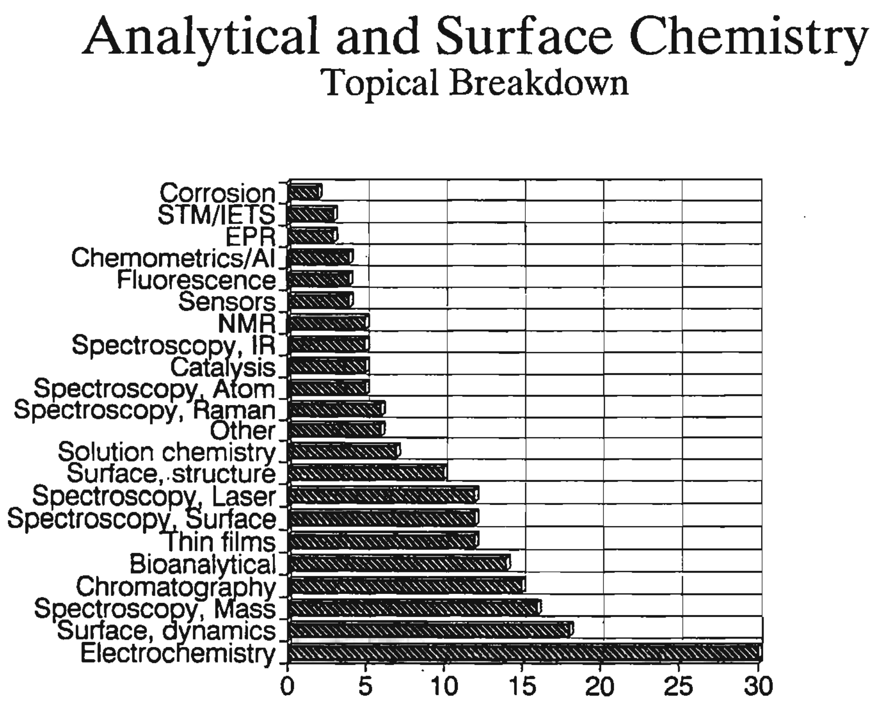


Chart 11: The topical breakdown of grants in FY 1990 in the Analytical and Surface Chemistry Program. Note that some grants have more than one topic.

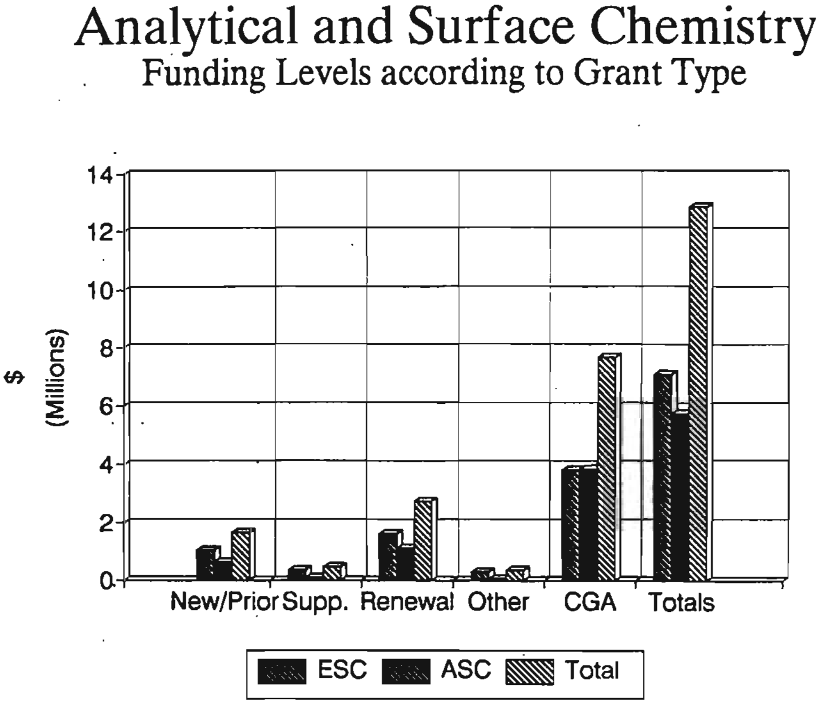


Chart 12: The distribution of funds between grant type and program element for FY 1990 in the Analytical and Surface Chemistry Program, in which ESC denotes electrochemistry and surface chemistry and contains all the surface chemistry grants (ASC denotes the rest of the program); CGA denotes the continuing grant award, the second and third year of funding of a normal three year grant; Supp denotes supplements to existing grants; and Prior denotes proposals from a principal investigator (PI) who was previously funded by NSF but had a renewal proposal declined.

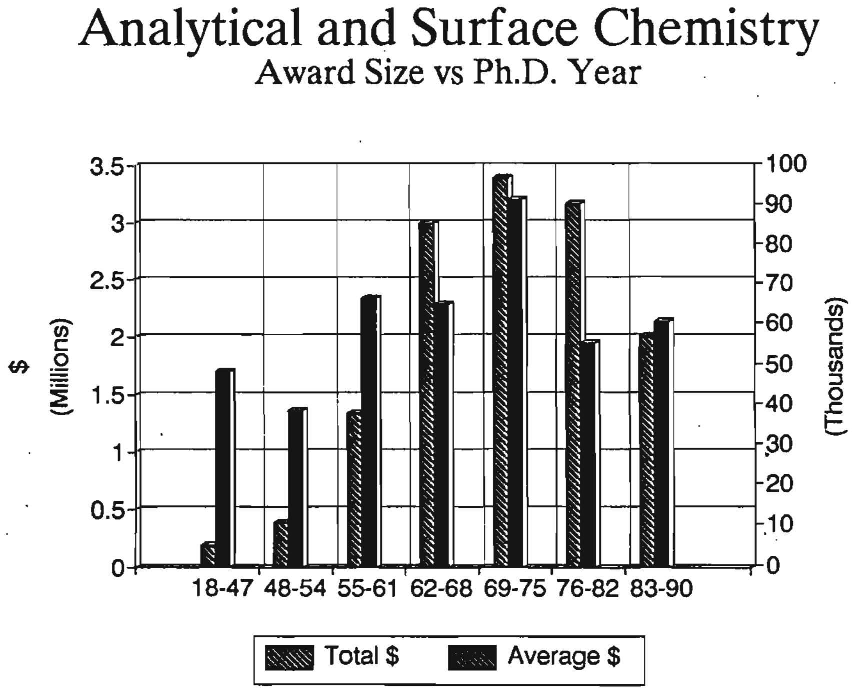


Chart 13: The relationship between the size of grant and the Ph.D. year of the principal investigator.

A3. THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

The Directorate of Chemistry and Materials Science of the Air Force Office of Scientific Research (AFOSR) has the mission to encourage and support fundamental research designed to increase knowledge and understanding, to stimulate the recognition of new concepts, and to provide for early exploitation by defense technology. The Directorate, led by Dr. Donald Ball, is the single manager for basic research in chemistry and structural materials for the Air Force.

The Directorate obtains and maintains for the Air Force a diversified program of research at Air Force laboratories as well as extramurally at university and industry laboratories. Sponsored research programs totaled approximately $16.6 million in FY 1991. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meetings, and sponsored symposia. The agents for this work are the Program Managers. The Directorate Program Managers, who are all located at AFOSR, Bolling AFB, Washington, DC, 20332-6448, and the program titles are as follows:

Chemical Reactivity and Synthesis: Dr. Fred Hedberg
Polymer Chemistry: Dr. Charles Lee
Inorganic Materials Chemistry: Capt. Thomas Erstfeld
Electrochemistry: Dr. John Wilkes
Theoretical Chemistry: Lt. Col. Larry Burggraf and Dr. Mark Gordon
Molecular Dynamics: Dr. Michael Berman
Metallic Structural Materials: Dr. Alan Rosenstein
Ceramics and Nonmetallic Structural Materials: Lt. Col. Larry Burggraf

For more than two decades, the Directorate has featured a strong program in Surface Chemistry. Within the past year, we have reorganized the Directorate to accommodate a strengthened materials emphasis. As part of that reorganization, we have combined the Surface Chemistry Program and the inorganic materials portion of the ultrastructure materials program created by the late Dr. Donald Ulrich into a single Inorganic Materials Chemistry Program.

I. INORGANIC MATERIALS CHEMISTRY, Capt. Thomas Erstfeld

The inorganic materials chemistry program supports basic research for synthesis and processing of structural materials and thin films.

Structural materials research encompasses multifunctional ceramics, solution ceramics, glasses, ultrastructure processing of ceramics and electronic/electrooptic materials, and oxidation-resistant carbon/carbon composites. The goal of this research is to produce structural, optical, and electronic materials that perform better at lower cost than do currently available materials. These improved materials can be used in systems for both the space and aerospace environments.

Thin-film research deals with control of chemical reactions at surfaces and interfaces. This research includes (1) the processing and characterization of electronic and electrooptic materials that are essential to future information, communication, and command and control systems; (2) the chemical control of friction on surfaces, which is necessary for the production of solid lubricants and bearings essential to future aerospace systems that will be subjected to high temperatures; (3) the study of hyperthermal surface reactions, common in the space environment and responsible for "shuttle glow," erosion, and charge exchange that limit systems performance and the operational life of spacecraft, with the goal of designing inert skins for space vehicles; and (4) the chemistry of catalysts for endothermic fuels to determine selectivity, efficiency, and rapid energy transfer to design a catalyst/supercritical fuel system for the high-temperature engines proposed for 21st-century aircraft.

The core surface chemistry portion of the Inorganic Materials Chemistry Program totals $1.54 million plus an additional $821 thousand through University Research Initiative (URI) Programs. The following chart outlines the FY 1992 investment in this program.

Surface Chemistry (FY 1992)

Topic	# PIs*	$K
Molecular Electronics/Optics	3	254
Novel Surface Techniques	1	130
Space Environment Effects	3	246
Carbon/Carbon Composite Oxidation	3	285
Endothermic Fuels Catalysis	1	202
Tribochemistry	4	421
URIs	5	821
TOTAL	20	2359
Excluding URIs	(15)	1538

*# PIs is the number of principal investigators.

However, other programs in the Directorate and in other AFOSR directorates also contribute research in interface phenomena. Examples of such efforts are given in the following program descriptions.

II. CERAMICS AND NONMETALLIC STRUCTURAL MATERIALS, Lt. Col. Larry W. Burggraf

Interest in nonmetallic structural materials is driven by a broad range of technological needs. Systems such as stoichiometric gas turbine engines and hypervelocity transatmospheric space planes are limited by the inability of current structural materials to function at high temperatures without degradation. Nonmetallic materials including ceramics such as borides, oxides, nitrides, carbides, and carbon/carbon composites, which have ionic and covalent bonding, have high binding energies and therefore high melting points. However, these materials are brittle and/or susceptible to oxidation.

We seek a fundamental understanding of how the physical and chemical properties of a material result in the macroscopic properties of interest, such as toughness, strength, fatigue resistance, and oxidation resistance. An understanding of the high-temperature mechanical properties and methods of imparting toughness to brittle materials at high temperatures is of great interest. The issues of interface phenomena and control in heterogeneous systems are also of interest. We seek better understanding of the role that oxidation protection debonding coatings play in the mechanics of composites. We want to understand the processing-microstructure-properties relationships in these materials. Of specific interest are novel precursors for ceramic matrix composites and carbon/carbon that allow control of the microstructure and provide an atomic-level distribution of dopants in the composite. A better understanding of the relationship between the electronic structure (e.g., atomic positions and band structure) and the physical properties, especially the mechanical properties, is of great interest. We seek proposals to perform innovative research to further our understanding of these issues.

III. ELECTRONIC DEVICES, Dr. Gerald L. Witt, Device Issues; Maj. Gernot S. Pomrenke, Materials Issues

The research program encompasses a wide variety of advanced electronic structures and devices, primarily fabricated from compound semiconducting materials. A range of materials systems (e.g., GaAs, InP, Si-Ge alloys on Si, the antimonides, and heteroepitaxial materials) and devices (such as pseudomorphic high electron mobility field effect transistors, heterojunction bipolar transistors, and resonant tunneling structures) are of interest—especially those structures exploiting quantum mechanical effects. The use of Si-Ge alloys for device applications is of particular interest. Special focus is placed on the understanding and applications of so-called "low temperature" GaAs and related layers. Research efforts are sought in approaches to wafer-level integration such as selected area heteroepitaxy, the use of patterned substrates, and the lift-off layer technique.

IV. SEMICONDUCTOR MATERIALS, Maj. Gernot S. Pomrenke and Dr. Gerald L. Witt

Air Force electronic and photonic signal processing, communications, surveillance, and electronic warfare systems require continual improvements in performance. This research program is directed toward developing advanced electronic and photonic materials to provide the required improvements in future Air Force electronic and photonic systems. In particular, we seek to generate the fundamental knowledge and the materials data base required for the growth and use of novel, as well as existing, electronic and photonic materials and structures. No single electronic material has the combination of properties required for all applications, so several classes of semiconductor materials, including heterostructural combinations, are currently under investigation. Similarly, several classes of photonic materials, including semiconductor heterostructures and nonlinear optical magnetooptical materials, are also under investigation. There is a growing interest in pushing toward a higher level of material integration with emphasis on selective-area epitaxy and growth on patterned or nonplanar substrates.

Compound semiconductors such as GaAs and InP, the ternary alloy GaAlAs, and heterostructural combinations of such materials are the foundation of a whole new generation of ultrahigh-speed, high-frequency digital and microwave devices and are being investigated in this effort. These materials provide the electronic and optoelectronic properties necessary for advanced information and signal processing applications and for optoelectronic communications. We are investigating these materials for potential use in detectors for the ultraviolet to infrared region, solid state laser, display, and emitter sources, and in infrared-active optoelectronic countermeasures.

An effort aimed at developing a Si and Si-Ge heterostructure technology for next generation digital computer, microwave, and optical sensor systems has recently begun and will continue. Efforts to develop combinations of Group II to VI and III to V materials and Group IV and Group III to V materials heterostructure technology for future device applications are also continuing. Novel concepts are being explored in quantum transport and structures. Interface issues and understanding of equilibrium and nonequilibrium growth processes through modeling are also important in heterostructure technology. Our overall emphasis in sponsored research is to combine materials science with solid state physics to investigate the fundamental aspects of growth, defects, and properties of multilayer semiconductor structures.

The program also addresses optical thin-film investigations. The aim is to gain a fundamental understanding of optical film properties using solid state physics and material science. Specific interests are in anti- and high-reflection coatings as they concern high-power laser applications and electrooptic sensors, nonlinear optical films, microscopy, and optoelectronic devices.

V. LIST OF PRINCIPAL INVESTIGATORS AND PROJECTS RELEVANT TO SURFACE PROCESSING

A. Kummel, The Effects of Molecular Orientation Geometry and Surface Antisotropy Upon Etching

S. J. Sibener, Dynamics of Gas-Surface Interactions

C. M. Lieber, Scanning Tunneling Microscopy Investigations of Metal Dichalcogenide Materials

E. Matijevic, Colloid and Interface Chemistry Aspects of Ceramics

B. H. Cooper, Resonant Charge Transfer in Hyperthermal Atomic and Molecular Ion-Surface Collisions

W. Ho, High Translational Energy Induced Reactions on Silicon

G. B. Hoflund, Development of an O-Atom Gun

L. L. Hench, Multifunctional Gel-Silica Optics

A. J. Gellman, Surface Species in Tribology

G. M. McClelland, Fundamental Studies of Friction, Lubrication and Wear by Atomic Force Microscopy

M. Trenary, The Structure and Reactivity of Boron Surfaces

J. Jonas, Fluids, Gels and Glasses Under Extreme Conditions of Pressure and Temperature

P. C. Stair, Experimental and Theoretical Investigation of Photodissociation on MgO(001)

J. T. Yates, Jr., The Synthesis and Characterization of Tribophysical Layers on Diamond and Silicon Carbide Surfaces

P. C. Stair, Experimental Investigations and Molecular Dynamics Simulations of Radiation Induced Surface Damage

T. Engel, Fundamental Aspect of Plasma Processing

B. E. Koel, Surface Science and Modeling Studies of Endothermic Fuels Catalysis

A4. GLOSSARY OF ACRONYMS AND ABBREVIATIONS

AEM	analytical electron microscopy
AES	Auger electron spectroscopy
AFM	atomic force microscopy
ALT	accelerated life testing
APFIM	atom probe field ion microscopy
ARUPS	angle resolved ultraviolet photoelectron spectroscopy
ATR	attenuated total reflection
BET	Brunauer, Emmett, and Teller
BLE	bombardment induced light emission
CDP	compositional depth profiling
CVD	chemical vapor deposition
DIET	desorption induced by electronic transitions
DLC	diamond-like coating
EDX	energy dispersive X-ray analysis
EELS	electron energy loss spectroscopy
EIID	electron impact ion desorption
ELEED	elastic low energy electron diffraction
EM	electron microscopy
EMP	electron microprobe (analyzer)
EPMA	electron probe microanalysis (analyzer)
ER	electromagnetic radiation
ESCA	electron spectroscopy for chemical analysis (see also XPS)
ESD	electron stimulated desorption
ESDIAD	electron stimulated desorption ion angular distribution
EVA	ethylene vinyl acetate (copolymer)
EXAFS	extended X-ray fine structure spectroscopy
FAB-SIMS	fast atom bombardment-secondary ion mass spectrometry
FEM	field emission microscopy
FIM	field ion microscopy
FIMS	field ion mass spectrometry
FTIR	Fourier transform infrared (spectroscopy)
FWHM	full width at half maximum
GDMS	glow discharge mass spectrometry
GDOS	glow discharge optical spectrometry
G/S	gas/solid interface
HEED	high energy electron diffraction
HFS	hydrogen forward scattering spectrometry
HREELS	high resolution electron energy loss spectroscopy
HRTEM	high resolution transmission electron microscopy
HV	high vacuum
HVEM	high voltage electron microscopy
IAD	ion assisted deposition
IBAD	ion beam assisted deposition
IBED	ion beam enhanced deposition
IIR	ion induced radiation
ILEED	inelastic low energy electron diffraction
IMFP	inelastic mean free path
IMMA	ion microprobe mass analyzer

INS	ion neutralization spectroscopy
IR(S)	infrared (spectroscopy)
ISS	ion scattering spectroscopy
LAMMA	laser microprobe mass analysis
LB	Langmuir-Blodgett
LEED	low energy electron diffraction
LEEM	low energy electron microscopy
L/G	liquid/gas interface
LIMS	laser ionization mass spectrometry
L/L	liquid/liquid interface
LMP	laser microprobe
LPE	liquid phase epitaxy
LRS	laser Raman spectroscopy
L/S	liquid/solid interface
MBE	molecular beam epitaxy
ML	monolayer
MRIS	multiple reflectance infrared spectroscopy
MSSN	mass spectrometry of sputtered neutrals
NRA	nuclear reaction analysis
NREL	National Renewable Energy Laboratory
NSS	neutral scattering spectrometry
OMA	organized molecular assembly
PAI	post ablation ionization
PIXE	particle induced X-ray emission
PMMA	polymethylmethacrylate
PV	photovoltaic
PVD	physical vapor deposition
QCM	quartz crystal microbalance
QMS	quadrupole mass spectrometer
(RA)IR	(reflection absorption) infrared
RBS	Rutherford backscattering spectroscopy
RGA	residual gas analysis
RHEED	reflection high energy electron diffraction
SA	self assembly
SALI	surface analysis by laser ionization (of sputtered neutrals)
SAM	scanning Auger microscopy or self assembled monolayer
SARISA	surface analysis by resonance ionization of sputtered atoms
SBEC	single binary elastic collision
SCANIIR	surface compositional analysis by neutral and ion impact radiation
SE	spectroscopic ellipsometry
SECS	solar energy conversion systems
SEM	scanning electron microscopy
SERS	surface enhanced Raman spectroscopy
SEXAFS	surface extended X-ray fine structure
SFE	surface free energy
SFG	sum frequency generation
S/G	solid/gas interface
SHEED	scanning high energy electron diffraction
SHG	second harmonic generation
SIMA	secondary ion mass analyzer

SIMS	secondary ion mass spectrometry
S/L	solid/liquid interface
S/N	signal-to-noise ratio
SNMS	secondary neutral mass spectrometry
S/S	solid/solid interface
STEM	scanning transmission electron microscopy
STM	scanning tunneling microscopy
STS	scanning tunneling spectroscopy
S/V	solid/vacuum interface
TD(MS)	thermal desorption (mass spectrometry)
TED	transmission electron diffraction
TEM	transmission electron microscopy
TOF-AP	time-of-flight atom probe
TOF-MS	time-of-flight mass spectrometry
TOF-SIMS	time-of-flight secondary ion mass spectrometry
TPD	temperature programmed desorption
UHV	ultrahigh vacuum
UPS	ultraviolet photoelectron spectroscopy
UV	ultraviolet
VHV	very high vacuum
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy (see also ESCA)
XRD	X-ray diffraction
XRF	X-ray fluorescence

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Dearborn, Michigan

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