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FWP Executive Summaries Basic Energy Sciences Materials Sciences Programs (SNL/NM)

G. A. Samara

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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FWP EXECUTIVE SUMMARIES

BASIC ENERGY SCIENCES
MATERIALS SCIENCES PROGRAMS
(SNL/NM)

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January 1997

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DISCLAIMER

I. Budget

Basic Energy Sciences/Materials Sciences Funding for FY96-99
Sandia National Laboratories - Albuquerque, New Mexico

Active Programs	Title	AFP FY96 ($K)	AFP FY97 ($K)	AFP FY98 ($K)	Projected FY99 ($K)
KC020101	Physics & Chemistry of Ceramics	1025	768*	1016	1067
KC020102	Science of Adhesion	447	424	445	467
KC020102	Wetting and Flow of Liquid Metals...	257	275	289	303
KC020103	Energetic Particles Synthesis...	767	732	769	807
KC020103	Advanced Growth	361	333	350	368
KC020105	Artificially-Structured Semiconductors	465	430	452	475
KC020105	Field-Structured Composites	160	156	164	172
KC020105	S&P Center (Performance Meas.)	88	83	88	92
KC020202	Tailored Surfaces for Materials Application	527	497	522	548
KC020202	Materials Science and Physics of Tl-Ba-Ca-Cu-O Superconductors	505	477	501	526
KC020202	Compositionally-Modulated Semiconduct...	200	190	200	210
KC020205	Transport in Unconventional Solids	475	448	470	494
KC020205	Synthesis & Processing Center	75	71	129	135
KC020303	CVD Sciences	662	625	656	689
KC020303	Nanoclusters	285	269	282	296
	TOTAL	6299	5778	6333	6649
Equipment	- Programmatic	991	1058	1058	1058
	- Awards	50	100		

New Initiative Proposal

Localized Corrosion Initiation at Nanoengineered Defects in Passive Films.....700K**

*After reduction due to FY96 carryover.

**This activity proposed for FY99 start up could start in FY98 if funds become available.

Note: The PNGV Project on Metal-Ceramic Interfacial Reactions Project (KC0201050) are not included in the budget above.

II. Capital Equipment Requests

Requests (In Priority Order)

1. STM/AFM Apparatus for Nanoclusters Research **$150K**

Imaging of nanoclusters on atomically smooth, non-porous substrates such as MoS_2, graphite or mica is technically very difficult and time-consuming in transmission mode (e.g. TEM or HRTEM) since the substrates must be ion milled to less than 50 nm for good imaging. Our collaboration with Prof. David Kelley, Colorado State University has shown that STM or AFM is excellent in this regard. Since we plan on studying films of nanoclusters we need in-house capability to perform STM and AFM. A combination instrument with these capabilities would provide rapid feed-back to allow us to improve synthesis and processing conditions for depositing nanoclusters on a variety of substrates. We anticipate that the major catalytic applications of nanoclusters in the future will employ such deposited films.

2. Scanning Probe Microscope for Characterization of Surface Structure **$100K**

An in situ atomic force/scanning tunneling microscope is needed for characterization of strained layer Group IV materials. The real space imaging information provided by this technique is a critical addition to the information determined by our surface diffraction techniques. The instrument will be used to study strain-induced surface roughening, ion-assisted growth processes and cluster nucleation kinetics.

3. Dual Port Glove Box for Alkoxide Chemistry **$50K**

A very large effort is currently underway to develop and characterize unique mixed metal systems so that the properties of these solutions and the thin films generated from them can be understood and ultimately controlled. The isolated compounds supported by the Physics and Chemistry of Ceramics project contribute to a wide number of other projects currently underway. Glove-box time is at a premium and with as many as 10 people working on these projects, there is significant amount of time spent waiting. In addition to the principal investigators, many other users have expressed interest and use our facilities. By addition of another glove box, we will be able to maintain and exceed our current level of productivity on a number of areas which are maturing and assist other groups at Sandia with increased service.

4. Variable-Temperature Ultra-High-Vacuum Scanning Tunneling Microscope **$500K**

We have demonstrated that Atom Tracking/Scanning Tunneling Microscopy can be an important tool for assessing the fundamental rate determining processes controlling surface diffusion, crystal growth, and materials degradation. The key to performing atomic-scale measurements of surface kinetics using scanning probe microscopies is to choose a sample temperature at which the kinetic event rate is not he time scale of the data acquisition. The event rates at a given temperature are determined by the activation barriers. A process with a barrier of ~0.75 eV will occur at about 1 Hz at room temperature. Atom and cluster processes on semiconductor surfaces must overcome barriers that are typically about 1 eV, requiring

measurements performed at elevated sample temperatures. On the other hand, atomic diffusion on metal surfaces occurs already at cryogenic temperatures because of the much lower activation barriers.

Although, we can image semiconductor surfaces between room temperature at 600°C using our home-made STM, we are unable to access the low temperatures needed to study metallic or chemically modified semiconductor surfaces. This new instrumentation will provide us with the means to directly measure surface kinetic processes over the full range of temperatures from cryogenic to high temperature.

One of the key elements of our program is to use atomic-level measurement to validate and refine predictive models for surface dynamical processes. Our theoretical efforts involve calculations on a variety of materials systems ranging from adsorbates on metal surfaces to cluster formation and stability on semiconductor surfaces. If we are not able to access the full range of temperatures, we will not be able to provide the experimental support needed to achieve our materials modeling goals.

5. Surface-Force Apparatus (SFA) for Porous Materials **$150K**

Few examples exist of controlled measurements of microscopic forces relevant to the porosity of sol-gel and other porous materials. The surface-force apparatus now being marketed by several companies is a class of instruments that does just that. The classic geometry has molecularly smooth surfaces, such as mica, in close proximity under measured force; their spacing is often determined interferometrically. These devices, in many ways cousins to atomic force microscopes, are rapidly becoming laboratory standards for research into complex materials. The SFA will have a liquid cell suitable for surfactant and alkoxide solutions.

6. Manipulator for In Situ Pole Figure Measurements **$70K**

This manipulator is required on our new metal thin film deposition chamber so that we can perform pole figure measurements of film texture in the growth chamber. This will enable us to study the evolution of the texture with film thickness and understand the relationship between nucleation, film stress and texture evolution.

7. Electron Energy Analyzer for Spectroscopic LEEM **$400K**

Real-time investigations of phenomena such as nucleation and growth, self-organization processes, and the evolution of surface morphology using our newly acquired low energy electron microscope (LEEM) require extensive surface characterization for substrate preparation and analysis of deposited material. Although the LEEM provides a detailed picture of the surface structure and morphology, it does not, in its present form, provide any surface chemical information. This situation can be remedied by placing an electron energy analyzer in the projection column of the LEEM. The technique, known as spectroscopic LEEM, permits simultaneous chemical and structural analysis of objects observed in the LEEM image. By selecting a particular Auger electron peak with the energy analyzer, one can obtain a chemical map of a particular surface species observed in the LEEM image. Energy filtering is also desirable for all high-resolution imaging in that it eliminates unwanted scattered electrons. Our LEEM is designed to accommodate a commercially available electron energy analyzer.

Chemical identification of objects observed in LEEM images is essential for studying growth processes in heteroepitaxial systems, for locating impurity (surfactant) species on the surface, and for characterizing the surface cleanliness Without the spectroscopic capability offered by this analyzer, we will be hampered in our ability to interpret many of the LEEM images we are now obtaining. We currently must rely on experiments performed in other apparatus to estimate the concentration and location of surface adsorbates and segregated species. As with most experiments, LEEM requires complementary analysis techniques to realize the maximum amount of information from an experiment. Without this additional capability it is difficult for us to fully interpret the very exciting imaging capability of the LEEM.

8. UHV Load Lock System **$26K**

A load lock is required for transferring samples into our new metal thin film deposition chamber without breaking vacuum. This capability would allow us to prepare cleaner surfaces to understand the effects of surface preparation on nucleation and texture evolution in ultra-high purity metal thin films.

9. Data Acquisition System **$20K**

We will extend our transport facilities by building a Hall effect apparatus for 4-300K measurements in a 10T field. Most major equipment required for this facility is in place, including the superconducting magnet, dewar, and sample probe. However, we require a small amount of funding, $20K, for electronic measurement equipment to complete the data acquisition system.

III. General Programmatic Overview and Institutional Issues

A. Goals and Current Research

The goals of the BES Materials Sciences Program at Sandia National Laboratories/New Mexico (SNL/NM) are:

- Perform basic, forefront interdisciplinary research that also demonstrates relevance of basic science to technology.
- Choose programs which support DOE interests and are complementary to Sandia's multi-program laboratory mission.
- Perform research in a setting which enhances technological impact because of Sandia's spectrum of coordinated basic research, applied research and development engineering.
- Take advantage of a wide range of large, capital-intensive research facilities not usually found at universities.

Our BES Materials Sciences Program has the central theme of Scientifically Tailored Materials. The major objective of this program is to combine Sandia's expertise and capabilities in the areas of solid state sciences, advanced atomic-level diagnostics and materials synthesis and processing science to produce new classes of tailored materials as well as to enhance the properties of existing materials for U.S. energy applications and for critical defense needs.

Current core research in this program includes the physics and chemistry of ceramics synthesis and processing, the use of energetic particles for the synthesis and study of materials, tailored surfaces and interfaces for materials applications, chemical vapor deposition sciences, artificially-structured semiconductor materials science, advanced growth techniques for improved semiconductor structures, transport in unconventional solids, atomic-level science of interfacial adhesion, high-temperature superconductors, and the synthesis and processing of nano-size clusters for energy applications. In addition, the program includes the following three smaller efforts initiated in the past two years: (1) Wetting and Flow of Liquid Metals and Amorphous Ceramics at Solid Interfaces, (2) Field-Structured Anisotropic Composites, and (3) Composition-Modulated Semiconductor Structures for Photovoltaic and Optical Technologies. The latter is a joint effort with the National Renewable Energy Laboratory.

Considerable synergism exists among these program elements, and most of them share a number of common themes based on either the science or the use of common synthesis and processing approaches. These themes are: Synthesis and Processing, Epitaxial Growth, Surfaces and Interfaces, and the use of Energetic Beams. Several of the technical activities of the program have been incorporated into the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials.

Our interdisciplinary program utilizes a broad array of sophisticated, state-of-the-art experimental capabilities provided by other programs as well as this program. The major leveraged capabilities include several molecular beam epitaxy and chemical vapor deposition facilities, a broad range of materials synthesis and processing facilities, clean rooms for microfabrication and nanostructuring of materials, ion-beam accelerators, laser-based diagnostics, advanced optical and surface spectroscopies, unique combined high-pressure/low-temperature/high-magnetic-field facilities, and electron, scanning tunneling and atomic force microscopies.

B. New Initiative Proposal

This year we have submitted jointly with Brookhaven National Laboratory a new initiative proposal entitled **Localized Corrosion Initiation at Nanoengineered Defects in Passive Films**. The goal of this proposal is to gain new insight into the problem of localized corrosion initiation in passive metals. Our approach is based on the novel and unique application of nanofabrication techniques to simulate specific defect types in well-defined locations. Results from this program will ultimately lead to a detailed understanding of why corrosion is localized, which defect types dominate pit initiation, and what additional factors need to be included to obtain a complete fundamental description of the initiation process. A summary of the proposal is presented in Sec. VI., p. 20.

C. The DOE Center of Excellence For The Synthesis and Processing of Advanced Materials (CSP)

In addition to being involved in the technical program of CSP, Sandia is responsible for the overall coordination of Center activities. An overview of the Center and a description of the projects which constitute its current technical focus are given in Section IV, p. 11.

D. Interaction with DOE Technology Programs, Industry and Universities

Our DMS-funded program is strongly coupled to DOE technologies programs at Sandia and was in the past few years responsible fully, or in part, for the generation of a large number of cooperative research and development agreements (CRADAs) with industrial partners. We also have less formal collaborations with industry and broad collaborations with universities. A summary detailing the integration of our DMS program with DOE Technologies programs is provided in Section V, p. 18. Interactions with universities and industry are cited in the summaries of the individual program elements (Sec. VII-B).

E. Technical Program Highlights

The technical accomplishments of the Program during the past year are summarized in Section VII-B. Some of the significant accomplishments are described in Section VII-A.

F. Program Reviews

1. External Reviews

Sandia's Materials Science and Technology (MS&T) Council sponsors an annual external review of Sandia MS&T programs. This review looks into the motivation, organization, management and technical quality of the program. Although this review does not deal specifically with the BES/MS program, different elements of this program are included in this review every year. The 1996 review took place on February 13-14, 1996 and the 1997 review was held on January 29-30, 1997. The 1997 Review Panel members were: John Bravman (Stanford) chair, Paul Fleury (Univ. of New Mexico), Douglas Craig (Oak Ridge National Laboratory), Jane Alexander (DARPA), Christine Sloane (GM), Harry Leamy (Univ. of North Carolina), and Gary Werth (B. F. Goodrich Aerospace).

A major review of the BES/MS program is being planned for later in 1997.

2. DMS Management On-Site Visits

- On March 1, 1996 Dr. Yok Chen of DMS visited and reviewed Sandia programs supported by Metallurgy and Ceramics.

- On October 24, 1996 Dr. Jerry Smith of DMS visited and reviewed Sandia programs supported by Solid State Physics and Materials Chemistry.

3. In-House Management Reviews

Each element of our program is evaluated on a continuing basis with respect to objectives and performance by the responsible line management. Each involved participant is evaluated on his/her contributions in a formal annual review process with feedback.

G. Program and Personnel Changes

Tom Picraux became the new director of the Physical and Chemical Sciences Center replacing Peter Mattern who retired in July 1996. Much of the BES/MS program at SNL/NM is in Tom's organization.

Wilhelm Gauster replaced Tom as Manager of our Nanostructure and Semiconductor Physics Department. Wil, a physicist with over 25 years of service at Sandia, has broad experience in materials research as well as in the management of energy programs. Our BES/MS-funded research on Energetic Particle Synthesis and the Science of Materials, Advanced Growth Techniques and Artificially-Structured Semiconductors are under his purview.

Effective April 1996, Jeff Tsao became manager of our Chemical Processing Sciences Department in which the bulk of the work on the CVD Sciences program takes place. Jeff has a long history in materials synthesis and processing, and most recently was manager of the Semiconductor Materials Department. Jeff replaces Peter Esherick, who actually switched departments with Jeff. Peter

coordinated our BES program for a number of years, and will be looking for opportunities to apply the science base developed in the BES program to the more manufacturing/processing activities in his new Department. In a complementary fashion, Jeff brings much knowledge of practical issues in materials processing to his new position, and will continue to ensure that our basic research on CVD remains at the leading edge and has practical relevance as well. With the change in personnel, we have taken the opportunity to ask Mike Coltrin to coordinate the FWP and reporting activities for the CVD program. Mike has been one of the leaders of this program, has a broad overview of the research performed under it, and is committed to ensuring vitality and innovation in this research.

Jim Schirber, long involved in our BES/MS-funded superconductivity research, retired early in 1996. Jim made many significant contributions to our work on organic and high-temperature oxide superconductors.

Peter Green left Sandia for a faculty position at the University of Texas, Austin. His departure left a void in the glass dynamics project of our Physics and Chemistry of Ceramic program. However, this void was quickly filled by a strong collaboration with Peter in his new position.

Several post doc colleagues have left and have been replaced by new associates. The high flux of postdoctoral associates has been a source of invigorating thought and activity for the BES program.

We have redirected the compound semiconductor effort of our Advanced Growth Techniques program to the growth of GaN in a CVD reactor with use of advanced in-situ diagnostics (developed in this and other programs) to better understand the growth of this important material. Jung Han, a new member of our technical staff, is in charge of this effort. Robert Hwang from Sandia/California has been added to improve our morphological characterization of SiGe layers on Si. Bob is expert in AFM and STM, and this real space characterization of morphology is critical for relating stress relaxation measurements to morphological changes. In addition, a collaboration with Prof. L. B. Freund at Brown Univ. has been set up to compare the measured morphologies and stress reduction with results from finite element calculations.

The new Low Energy Electron Microscope (LEEM) which was purchased with FY95-96 BES capital equipment funds has been delivered and is producing results. This microscope and our recently-developed Atom Tracker put our surface science activities at the forefront of experimental approaches for understanding atomic-scale surface and interface processes.

H. Program Quality/Recognition

1996 was another excellent year in terms of the significant accomplishments and productivity of our DMS program (as detailed in Section VII of this Executive Summaries booklet) and in terms of the professional recognition received by our staff, both of which reflect on the quality of our BES program.

Peter Feibelman was the recipient of the 1996 Medard W. Welch Award of the American Vacuum Society. The Award recognizes Feibelman for his insightful predictions and explanations of surface phenomena based on first principles calculations. The work has covered a broad range of surface phenomena and is distinguished for its close coupling to experimental research.

Richard Brow was the recipient of the 1996 Gottardi Prize of the International Commission on Glass. The Prize recognizes Brow for fundamental research on structural dynamics of phosphate glasses. This prize is given annually for significant contributions by glass scientists under forty years of age. Brow is the first American to win it since its inception a decade ago. His research investigated the peculiar and important viscoelastic properties of phosphate glasses near their melting points. Unlike typical three-dimensional network glasses, phosphates are chainlike.

Richard Brow also received a 1996 R&D 100 Award for work related to his Gottardi Prize. This Award recognizes Brow for the development of a chemically durable, low melting point glass for aluminum-glass joining. Driven initially by a classified need in Defense Programs, the development of this alumino-phosphate glass was eventually applied by Sandia to sealing glasses in connectors for weapons, and it is currently licensed by aerospace companies who can now replace stainless steel components with light weight aluminum. The BES program contributed insights to the later-stage development, particularly in flow processes for the glass.

C. Jeffrey Brinker received a 1996 R&D 100 Award with Douglas Smith (Univ. of New Mexico and now Nanopore, Inc.) for the development of an ambient-pressure process to make ultralight aerogels. The new process promises to lower the cost of aerogel materials dramatically by removing the necessity to use supercritical drying at high pressure. Low cost aerogels could impact thermal insulation and dielectric materials markets among other areas. The BES program fostered the groundbreaking chemical and physical insights needed to manage capillary pressures during nonsupercritical drying.

Brian Swartzentruber was the winner of the 1996 BES Materials Sciences Award for Outstanding Scientific Accomplishment in Solid State Physics for development of Atom-Tracking Scanning Tunneling Microscopy for Direct Measurements of Surface Dynamics. This microscopy increases the time resolution for measuring dynamic surface events by more than a factor of 1000 over conventional imaging techniques. By locking onto and tracking individual, atomic-scale diffusion events, dynamics at single lattice sites can be measured.

Jess Wilcoxon, Paula Newcomer, David Bliss, Anthony Martino and George Samara were the winners of the 1996 BES Materials Sciences Award for Significant Implication for DOE-Related Technologies in Materials Chemistry for their work on Nanoclusters for Energy Applications. This research produced a variety of metal and semiconductor nanoclusters as potential inexpensive catalysts and solar photocatalysts with tailorable surface and optical properties. In addition to its technological potential, the work led to new physics and demonstrated the strong influence of dimensionality on quantum confinement.

John Curro shared the 1996 BES Materials Sciences Award for Outstanding Scientific Accomplishment in Materials Chemistry with collaborators at the Oak Ridge National Laboratory and the Univ. of Illinois Frederick Seitz Materials Research Laboratory for their work on Blends of Macromolecules with Nanophase Separation. This work developed a molecular level understanding of the factors that control the miscibility and the thermodynamic and material properties of polymer alloys using an integrated experimental/theoretical approach.

Brian Swartzentruber and Richard Cairncross, a recent Sandia post doc, now on the faculty at the Univ. of Delaware, received DOE's 1996 "Young Scientist" awards. Richard also won a 1996

Presidential Early Career Award for Scientists and Engineers. Cairncross made significant experimental and modeling contributions to our BES-funded research on sol gels and porous solids.

We also organized conferences, symposia, chaired sessions, wrote review papers, and presented numerous invited papers at national and international conferences (see individual program summaries in Section VII-B for details).

IV. The DOE Center of Excellence for the Synthesis and Processing of Advanced Materials (CSP)

Overview

The DOE Center of Excellence for the Synthesis and Processing of Advanced Materials (CSP) is a distributed center for promoting coordinated, cooperative research partnerships related to the synthesis and processing of advanced materials. It was established by DOE's Division of Materials Sciences, Office of Basic Energy Sciences and the DOE Laboratories in recognition of the enabling role of materials synthesis and processing to numerous fabrication- and manufacturing-intensive technologies. The participants include investigators from 12 DOE national laboratories, universities and the private sector. The Center has a technological perspective which is provided by a Technology Steering Group.

The current emphasis of the Center is on eight focused multilaboratory projects which draw on the complementary strengths of the member institutions in their ongoing research programs. These eight projects were selected on the basis of the following criteria: (1) scientific excellence, (2) clear relationship to energy technologies, (3) involvement of several laboratories, (4) strong existing or potential partnerships with DOE Technologies-funded programs, and (5) strong existing or potential "in-kind" partnerships with industry.

The eight projects are: (1) Metal Forming, (2) Materials Joining (3) Microstructural Engineering with Polymers, (4) Tailored Microstructures in Hard Magnets, (5) Processing for Surface Hardness, (6) Mechanically Reliable Surface Oxides for High Temperature Corrosion Resistance, (7) High Efficiency Photovoltaics, and (8) Design and Synthesis of Ultrahigh-Temperature Intermetallics.

The member laboratories of the Center are: Ames Laboratory (Ames), Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), Idaho National Engineering Laboratory (INEL), University of Illinois Frederick Seitz Materials Research Laboratory (UI/MRL), Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL). The Center also includes appropriate university grant research.

Objective

The overall objective of the Center is,

> *"To enhance the science and engineering of materials synthesis and processing in order to meet the programmatic needs of the Department of Energy and to facilitate the technological exploitation of materials".*

Synthesis and processing (S&P) are those essential elements of materials science and engineering (MS&E) that deal with (1) the assembly of atoms or molecules to form materials, (2) the manipulation and control of the structure at all levels from the atomic to the macroscopic scale, and

(3) the development of processes to produce materials for specific applications. Clearly, S&P represent a large area of MS&E that spans the range from fundamental research to technology. The goal of basic research in this area ranges from the creation of new materials and the improvement of the properties of known materials, to the understanding of such phenomena as diffusion, crystal growth, sintering, phase transitions, etc., in relation to S&P. On the applied side, the goal of S&P is to translate scientific results into useful materials by developing processes capable of producing high quality, cost-effective products.

The Center's Technology Steering Group

A Technology Steering Group (TSG) for the Center has been established. The role of TSG is to become familiar with the Center's technical activities and comment on their technological value, provide information from a technology perspective, help identify technological barriers, influence the direction of the Center's programs, and help develop ideas which can make the Center more effective.

Current TSG membership is as follows:

Member	Affiliation
Dr. David J. Beecy	DOE/Fossil Energy
Dr. Thomas C. Clarke	IBM-Almaden
Dr. David W. Johnson, Jr.	AT&T Bell Labs
Dr. Hylan B. Lyon	Marlow Industries
Dr. Neil E. Paton	Howmet
Dr. Charles Sorrell	DOE/Energy Efficiency & Renewable Energy
Dr. John Stringer	Electric Power Research Institute (EPRI)

Materials and Processes Focus of the Center

The current emphasis of the Center is on the eight projects cited above.

Each of the projects is coordinated by an appropriate representative from one of the participating institutions. The overall Center coordinator is:

George A. Samara: (SNL/NM)
Phone: (505) 844-6653
Fax: (505) 844-4045
E-mail: gasamar@sandia.gov

A brief description of each project follows:

Metal Forming

Participating Labs:	Ames, LBNL, LLNL, LANL, ORNL, PNNL, SNL/CA, SNL/NM
Coordinator:	Michael Kassner (Oregon State)
Phone:	(541) 737-7023
Fax:	(541) 737-2600
E-mail:	kassner@engr.orst.edu

This project is motivated by the goal of improving fuel efficiency in transportation systems. Achieving this goal requires the use of light weight structural materials which in turn necessitates consideration of aluminum alloys. Unfortunately, compared to steels, Al alloys are more expensive.

The first objective of this project is a scientific understanding of phenomena relating to the forming of aluminum alloys for commercial (especially automotive) applications. This particularly includes recrystallization, which is both poorly understood fundamentally, and poorly predicted during industrial processing. Recrystallization is basically a process by which the material softens by forming new, relatively defect-free, crystallites. The study of recrystallization phenomena includes understanding the precursor states of microstructures.

The second objective is developing constitutive equations that will predict, over a complicated thermal and mechanical process, such as will be experienced during industrial processing, the mechanical behavior of aluminum alloys for automotive applications. The equations will consider recrystallization, texture, hardening and dynamic recovery (a less dramatic softening process than recrystallization). No set of constitutive equations has yet effectively modeled these phenomena. The scientific underpinning of the first objective could allow more realistic and versatile constitutive equations.

Materials Joining

Participating Labs:	Ames, INEL, LBNL, LLNL, ORNL, PNNL, SNL/CA, SNL/NM
Coordinator:	R. B. Thompson (Ames)
Phone:	(515) 294-9649
Fax:	(515) 294-4456
E-mail	thompsonrb@ameslab.gov

Materials joining is an enabling technology in virtually all industrial sectors, and often the reliability of joints is the factor that limits performance. Welding is an old technology, but weld failures are common and some technologically important materials such as aluminum alloys are difficult to weld. Advanced high temperature ceramics have tremendous potential in energy and related technologies, but there are no reliable methods of joining them. These realities provide the motivation for this project.

The project consists of two tasks. The first entitled "*The effects of Gradients on Weld Reliability and Performance,*" uses advances in experimental, analytical and computational tools to develop an integrated and quantitative understanding of the origin and extent of gradients in composition, stress, microstructure and properties which occur during various welding processes. Strategies will also be developed to control these gradients which are often the cause of failure. Initial emphasis is on Al-Cu alloys and on Fe-Ni-Cr alloys.

The second task, "*Ceramics and Dissimilar Materials Joining,*" focuses on critical issues in the non-welding joining area which include property mismatch between members to be joined; use temperature limitation; joining temperature limitation; poor wetting, adhesion and/or chemical bonding; potential for use in the field; and manufacturing and/or joint reliability. Some of the initial emphasis is on silicon carbide joining, an area of strong interest to the Fossil Energy and Energy Efficiency/Renewable Energy Offices. This part of the work is being done in collaboration with research sponsored by the Continuous Fiber Ceramic Composites Program, Office of Industrial Technologies, Office of Energy Efficiency and Renewable Energy.

Microstructural Engineering with Polymers

Participating Labs:	Ames, BNL, INEL, UI/MRL, LBNL, LLNL, PNNL, SNL/NM
Coordinator:	Gregory J. Exarhos (PNL)
Phone:	(509) 375-2440
Fax:	(509) 375-2186
E-mail:	gj_exarhos@pnl.gov

Ongoing fundamental research involves the design, development, and implementation of advanced processing protocols which direct the evolution of hierarchical microstructures in mixed phase composites, alter materials properties, and induce multifunctionality. This can be achieved by combining constituents at the molecular level in order to impart properties inaccessible by conventional processing routes. The project is not simply directed toward polymer synthesis, but involves the use of engineered polymers or macromolecules in processing methods designed to produce targeted architectures or promote mixing in ceramics, polymers, glasses or mixed multicomponent phases. An integral thrust area within the project involves materials properties modeling by means of semi-empirical approaches based upon small model systems. Verification of the modeling is based on scattering and physical properties measurements for these model systems and provides guidelines for further development of modified materials processing routes. This project is comprised of two tasks: (1) engineered porosity and (2) blends, composites and alloys. Recent activities have been focused upon influencing transport phenomena (ion/molecule diffusion, electron transport, heat flow) in polymer-tailored materials. The program provides a fundamental underpinning for the development of new materials to support electric power, chemical separations, thermal insulation, automotive, membrane, sensor, and catalysis technologies.

Tailored Microstructures in Hard Magnets

Participating Labs:	Ames, ANL, BNL, INEL, LBNL, LLNL, LANL, ORNL
Coordinator:	Bob Dunlap (ANL)
Phone:	(630) 252-4925
Fax:	(630) 252-4798
E-mail:	bddunlap@anl.gov

Improvements in the properties of permanent (or hard) magnetic materials can lead to lighter, more efficient and longer life motors for energy, transportation and many other industries. A figure of merit for permanent magnet materials is the maximum energy product, W. In some of the best current commercial materials W is ≤50% of its theoretical value. The problem is generally attributed to a lack of understanding of the role of microstructure in determining magnetic properties. Other limitations of current commercial magnetic materials are relatively poor mechanical and corrosion-resistant properties. These properties are also determined largely by microstructure.

The overall objective of this project is to improve hard magnets by understanding, in terms of the microstructures achieved, the magnetic and mechanical properties of materials produced by a number of synthesis and processing (S&P) approaches.

Initial focus is on the technologically important material $Nd_2Fe_{14}B$ as a model system. Specifically, this material is being produced in single crystal, powder, bulk and thin film forms and characterized

by state-of-the-art tools. The microstructures developed by the different S&P methods are being compared and modeled. The relationships between microstructure and domain wall pinning, magnetic properties and mechanical properties are being determined. The ultimate goal is to identify S&P approaches which optimize material properties for specific applications.

Processing for Surface Hardness

Participating Labs:	ANL, BNL, LBNL, LLNL, LANL, ORNL, SNL/CA, SNL/NM
Coordinator:	J. B. Roberto (ORNL)
Phone:	(423) 576-0227
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There exists a broad range of applications for which the ability to produce an adherent, hard, thin, wear-resistant coating plays a vital role. These applications include engine and machine components, orthopedic devices, textile manufacturing components, hard disk media, micromachined sensors and actuators, optical coatings, and cutting and machining tools (e.g., punches, taps, scoring dies, and extrusion dies). Emphasis is placed on development and improvement of processes which are environmentally benign and which provide flexible control over the surface structure and chemistry.

Plasma-based processing is an important component of processes used for the applications listed above. The ability to provide flux, energy, and temporal control of a variety of ions, which is characteristic of plasma-based processing, provides the means to tailor surface hardness and other tribological properties.

The goal of the project is to address critical issues which limit the use of plasma-based processing for surface hardness. Initial emphasis is on plasma ion immersion processing (PIIP), a relatively inexpensive non-line-of-sight-implantation process capable of treating complex-shaped targets without complex fixturing, and on boron-based superhard coatings where the focus is on cubic boron nitride and boron suboxides.

Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance

Participating Labs:	ANL, INEL, LBNL, LLNL, ORNL
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Protection from corrosion and environmental effects arising from deleterious reactions with gases and condensed products is required to fully exploit the potential of advanced high-temperature materials designed to improve energy efficiency and minimize deleterious environmental impact. The resistance to such reactions is best afforded by the formation of stable surface oxides that are slow growing, sound, and adherent to the substrate and/or by the deposition of coatings that contain or develop oxides with similar characteristics. However, the ability of brittle ceramic films and coatings to protect the material on which they are formed or deposited has long been problematical, particularly for applications involving numerous or severe high temperature thermal cycles or very aggressive environments. This lack of mechanical reliability severely limits the performance or

durability of alloys and ceramics in many high-temperature industrial applications and places severe restrictions on deployment of such materials. The beneficial effects of certain alloying additions on the growth and adherence of protective oxide scales on metallic substrates are well known, but satisfactory broad understandings of the mechanisms by which scale properties and coating integrity (that is, corrosion resistance) are improved by compositional, microstructural, and processing modifications are lacking.

The objective of this task is to systematically generate the knowledge required to establish a scientific basis for the design and synthesis of improved (slow growing, adherent, sound) protective oxide coatings and scales on high temperature materials without compromising the requisite bulk material properties. Specific objectives are to (1) systematically investigate the relationships among substrate composition and properties and scale/coating failure using a mix of relevant microstructural and mechanical characterization techniques and modeling, and (2) identify conditions leading to more damage-tolerant coatings and scales that are amenable to legitimate synthesis routes. The initial emphasis is on alumina scales and coatings, and the work is co-sponsored by the Office of Advanced Research, Fossil Energy Program. Some of the work in the project is also in collaboration with the Electric Power Research Institute (EPRI).

High Efficiency Photovoltaics

Participating Labs:	Ames, ANL, BNL, INEL, UI/MRL, LBNL, LLNL, NREL, ORNL, PNNL, SNL/CA, SNL/NM, Caltech, MIT, SUNY, U.Florida, UCSB, U.Utah, Washington State U.
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Advances in the technology of solar photovoltaic (PV) energy conversion are critically dependent on the fundamental understanding of the synthesis and properties of the materials that compose solar cells. Reduced cost, improved conversion efficiency, and long-term stability are the major objectives of the DOE Photovoltaics Program. Thin-film semiconductor materials and device technologies are key to achieving these objectives. Currently, there are several important classes of thin-film PV materials at various stages of research and development, but in all cases there is a lack of understanding of the fundamental scientific issues associated with each of these technologies. Therefore, this program is motivated by the scientific exploration of new solid-state physics as it relates to photon absorption and carrier transport, novel materials synthesis techniques, the characterization and control of defect structures, and ultimately designs of new material architectures.

The project is focused on two areas: (1) Silicon-Based Thin Films, in which key scientific and technological problems involving amorphous and polycrystalline silicon thin films will be addressed; and (2) the Next Generation Thin Film Photovoltaics, which will be concerned with the possibilities of new advances and breakthroughs in the materials and physics of photovoltaics using non-silicon-based materials.

Design and Synthesis of Ultrahigh-Temperature Intermetallics

Participating Labs:	Ames, ANL, INEL, LANL, LBNL, LLNL, UI/MRL, ORNL, and SNL/CA		
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This recently approved Project has the ultimate goal to develop scientific principles to design new-generation intermetallic alloys for structural applications at temperatures at and above 1400°C. The initial thrust is on Mo_5Si_3-base alloys which possess outstanding high-temperature strength and oxidation resistance (when alloyed with boron). The broad objective is to generate the knowledge required to establish a scientific basis for the processing and design of transition-metal silicides with improved mechanical and metallurgical properties at ambient and elevated temperatures.

The Project is organized into three major tasks as follows: (1) first-principles calculations, atomistic simulations, and mechanical modeling; (2) experimental study and correlation of structure and properties; and (3) innovative materials processing and fabrication of high-purity materials.

The Project builds on base programs funded by BES at all participating institutions; by Fossil Energy Advanced Research and Technology (AR&TD) programs at ANL, INEL, and ORNL; and by Energy Efficiency Advanced Industrial Materials (AIM) programs at Ames Laboratory, LANL, and ORNL.

V. Interaction with DOE Technology Programs, Industry and Universities

A. Integration with DOE Technologies Programs

One of the primary goals of our DMS program at Sandia is to choose research areas which support DOE technology interests and are complementary to the Laboratories' multi-program mission. Consequently, all DMS-supported research is strongly integrated with our other R&D activities in support of defense, energy and environmental programs. Specific areas where DMS research impacts DOE technologies needs include: materials synthesis and processing, long-term materials stability and reliability of components, reduction of friction and wear, control of impurities and defects in microelectronics and photovoltaics, radiation hardness of microelectronics and photonics, improved materials joining, advanced diagnostics and sensors, advanced separations membranes and novel catalysts and environmental remediation concepts.

The following table summarizes the relationship of our BES program to DOE Technologies programs or interests.

BES/MS Project	Related/Interested DOE Technologies	Relationship
• Physics and Chemistry of Ceramics	FE/METC	Separation membranes (complementary funding)
Assink et al	DP	Aerogels, powder compaction, ceramic processing, composites (complementary funding)
• Atomic Level Science of Adhesion *Michalske et al*	DP	Bonding strength and reliability (complementary funding)
• Wetting and Flow of Liquid Metals and Amorphous Ceramics at Solid Interfaces *Michalske et al*	FE DP	Ceramic joining Metal and ceramic joining (complementary funding)
• Energetic-Particle Synthesis and Science of Materials	DP	Hard surface layers; plasma processing (complementary funding)
Barbour et al	MFE	First wall materials and diagnostics
• Advanced Growth Techniques and the Science of Epitaxy *Chason et al*	DP	MBE growth and in-situ monitoring (complementary funding)

BES/MS Project	Related/Interested DOE Technologies	Relationship
• Artificially-Structured Semiconductor Materials Science *Gourley et al*	EE DP	Photovoltaic materials Photonic materials for devices (complementary funding)
• Physics and Chemistry of Novel Superconductors *Venturini et al*	EE/STEPS DP	Phase equilibria and processing of Tl high Tc superconductors Materials for high Tc devices (complementary funding)
• Tailored Surfaces and Interfaces for Materials Applications *Kellogg et al*	DP	Surface/interface stability; aging, reliability (complementary funding)
• Transport in Unconventional Solids *Aselage et al*	MFE EE DP	First wall materials High temperature thermoelectrics Neutron detectors; thermoelectrics (complementary funding)
• CVD Sciences *Coltrin et al*	DP EE	Materials growth; reactor design; in-situ diagnostics (complementary funding) Photovoltaic materials
• Synthesis and Processing of Nanoclusters for Energy Applications *Wilcoxon et al*	FE/PETC DP EM	Coal catalysis Novel device concepts (complementary funding) Waste remediation (complementary funding)
• Field-Structured Anisotropic Composites *Martin et al*	EE DP	Vibration damping, controls, clutches Controls, vibration damping, component encapsulants (complementary funding)

B. Industrial and University Interactions

The research results and capabilities of our DMS-sponsored program were in the past several years responsible fully or in part for the generation of over 30 cooperative research agreements or contracts with industrial partners. Although many of the CRADAs have been completed or terminated, we still have numerous less formal, but significant industrial interactions and/or technology transfer activities. We also have numerous university interactions. Some of these interactions are cited in the program summaries in Sec. VII-B.

VI. New Initiative Proposal

Localized Corrosion Initiation at Nanoengineered Defects in Passive Films

Principal Investigators

SNL/NM: R. G. Buchheit, N. A. Missert, J. P. Sullivan, K. R. Zavadil, J. C. Barbour, J. A. Floro, G. L. Kellogg. **BNL:** H. Isaacs

Motivation and Objectives

The goal of this proposal is to gain new insight into the problem of localized corrosion initiation in passive metals. Our approach is based on the novel and unique application of nanofabrication techniques to simulate specific defect types in well-defined locations. Results from this program will ultimately lead to a detailed understanding of why corrosion is localized, which defect types dominate pit initiation, and what additional factors need to be included to obtain a complete fundamental description of the initiation process. Our approach brings together expertise and state-of-the-art facilities from the diverse fields of corrosion science, thin film electronic materials, and surface science. The key aspect of this study is that the identity, location and characteristics of the defects in question will be well specified. Advanced *in-situ* electrochemical, dielectric and local chemical analyses will be used to investigate pit initiation in a way that has not been previously possible. Defects will be created using UHV thin film deposition, selective area ion implantation, local electron stimulated desorption/halide adsorption, and hot electron-induced dielectric breakdown. Our knowledge of the precise defect type will enable electrochemical characterization of pit initiation on a defect specific basis. Nanoengineered defects will be used to identify a possible correlation between local dielectric properties and pit initiation, study morphological changes at initiation sites prior to pitting by *in-situ* AFM, and explore the role of local variations in oxide chemistry on pit initiation with XANES. It is the recent advances in nanoscale fabrication and characterization that make possible our innovative approach to this long-standing problem at a time when aging infrastructure requires the ability to make accurate life predictions.

Program Highlights

Localization of Anion Adsorption: The action of aggressive anions, such as Cl, is known to play a role in pit initiation in passive metals. The factors responsible for driving Cl adsorption to occur at a specific site will be investigated through the use of controlled defects at the oxide surface, and nanoengineered defect arrays within the oxide layer or at the oxide-metal interface to force local Cl adsorption. Local Cl adsorption will be monitored using our UHV/electrochemical test system combined with Auger mapping. Electrochemical analysis of these defect arrays will determine whether the local Cl adsorption sites act as pit initiation sites.

Point Defect and Electron Transport Factors: A spatial variation in point defect flux within the oxide layer may cause pit initiation to be localized. These local initiation sites may be associated

with dielectric breakdown. We will create controlled defects within the oxide layer using ion implantation and deposited oxide structures in order to locally influence point defect fluxes. The role of point defects in localized corrosion initiation will be assessed using electrochemical measurements of pit induction time and dependence on electrochemical environment. The role of dielectric breakdown in pit initiation will be studied using hot electron emission microscopy to identify breakdown sites and look for a possible correlation with pit initiation sites. Dielectric characterization techniques will be used to assess electrical breakdown mechanisms and noise spectrum and correlate these with electrochemical noise measurements and current triggers preceding pit initiation.

Corrosion Mechanisms Related to Defects and Heterogeneities at the Oxide-Metal Interface: The mechanism for localized corrosion initiation at second phase particles will be investigated by decoupling oxide defects from metal heterogeneities. We will artificially simulate second phase particles at the oxide-metal interface using ion implantation or local Cu deposition and annealing, and compare the corrosion response using deposited oxides (where the defect structure is uniform) to passive oxides (which should contain local defects associated with the metal heterogeneity). The role of local impurity enhanced oxide dissolution on large area defect arrays will be studied using *in-situ* XANES. Oxide defect-driven corrosion processes will be decoupled from electrochemical activity by comparing the corrosion response of samples with controlled grain boundary densities with deposited oxides to those with passive oxides. Critical size effects will be studied using engineered defect structures with dimensions ranging from less than 0.1 μm to over 10 μm.

Electrochemical Signatures of Defects: The electrochemical signature of pit initiation at specific defect types will be determined. Corrosion initiation events will be monitored prior to, during, and following stable pit initiation using *in-situ* AFM localized at nanoengineered defects. The presence or absence of interaction between corrosion pits will be determined using an array of miniature isolated electrochemical electrodes with one defect or defect type per electrode.

Budget

We request $700K per year for a minimum of three years to carry out the proposed research, which includes $100K per year to be allocated to BNL.

VII. Research Program Summaries

A. Significant Accomplishments

MOCVD of Sb-Based Materials

KC 02 03 03

Scientific Accomplishment

We have applied our advanced vertical-flow rotating-disk reactor (RDR) and *in-situ* optical reflectance monitoring tools, to the MOCVD growth of antimonide-based materials. The new approaches and tools developed under our BES program have greatly alleviated the impediments to such growth. Sharp AlAsSb/InAs heterojunctions, necessary for a variety of applications, cannot be grown in conventional horizontal-flow reactors due to Al carryover from the AlAsSb into the InAs layer. Aluminum predeposition and, thus, fatal Al-contamination between AlAsSb/InAs layers are eliminated in the RDR, enabling us to demonstrate, for the first time, continuous MOCVD growth of multiply stacked LED and laser heterostructures. In addition, our *in-situ* optical reflectometry was used to simultaneously monitor growth rates and morphology changes during MOCVD, and to optimize the growth process. We have now demonstrated reproducible growth of thick (up to 5 μm) layers of $AlAs_xSb_{1-x}$ (x = 0.165) and $GaAs_xSb_{1-x}$ (x = 0.088) on InAs substrates with the ±0.4% control of composition required for high-quality, lattice-matched, zero-accumulated-stress devices. In conventional AlGaAs materials, control of the Al:Ga ratio requires only control of the relative Al and Ga precursor partial pressures, due to the great over-pressure of the group V precursors. In AlAsSb alloys, however, control of the As:Sb ratio is much more difficult and much more crucial, since it controls the degree to which lattice-matching with the substrate, and smooth surface morphologies, can be achieved.

Significance — Narrow-bandgap semiconductors such as InSb, InAs, GaSb, AlSb (and associated ternary and quaternary combinations) have unique physical properties which can be tailored to a host of applications. These applications include sensitive and robust magnetoresistance and Hall effect devices for ignition-timing motion sensors that are already being used to maximize fuel economy and minimize fuel emissions in automobiles. The applications may someday include compact mid-infrared optical devices (lasers, LEDs and detectors) for environmental sensing of atmospheric pollutants and for real-time sensing and optimization of fossil-fuel combustion. Our improvements in material quality in this system, demonstrated by photoluminescence (optical quality), x-ray defraction (crystalline quality) and optical microscopy (surface morphology), promise to accelerate realization of these future applications of antimonide-semiconductor-based materials.

Performers: K. C. Baucom and A. A. Allerman (Sandia National Laboratories/NM).

Measurement and Modeling of Monolayer Shear Dynamics

KC 02 01 02

Scientific Achievement

By coupling novel Acoustic Wave Damping experiments with molecular dynamics simulations, we have shown that quantitative changes in monolayer viscoelasticity can be related to specific changes in atomic scale structure. Our experimental technique measures the elastic energy storage and dissipative loss within a molecular film chemically bonded to the electrodes of a high-frequency quartz crystal resonator undergoing periodic shear deformation. By comparing structurally-related, two-dimensionally ordered, alkane thiol monolayers, we found that the elastic shear modulus of the monolayer varies systematically as a function of alkane chain length and shear rate. For molecules having twelve to eighteen carbon atoms, the film elastic shear modulus increases with chain length, from ~0.01 MPa to ~0.1 MPa, respectively. Monolayers composed of short chain molecules are less well ordered and exhibit a modulus increase with shear rate; longer chain alkane films do not exhibit this shear rate dependence.

Molecular dynamics simulations enable us to relate measured viscoelastic properties to atomic scale bonding and structure. For a representative, perfectly ordered monolayer of sixteen-carbon alkane thiol molecules, applying a static shear stress to the film yields theoretical elastic moduli (10-100 MPa) that exceed experimental results. However, inertially shearing the film by a high-frequency lateral translation of the substrate (analogous to the experiment) reveals that the ensemble response involves azimuthal molecular rotation about the surface normal, rather than simple molecular libration. The unexpected quasi-rotational motion is energetically preferable to one-dimensional shear and can account for a lower elastic modulus. Further simulations predict a chain-length dependence and show that the introduction of defects into the monolayer leads to energy dissipation that is otherwise absent in the perfectly ordered layer.

Significance — Self-assembled monolayers are not only good model systems for studying the relationship between atomic-scale structure and interfacial viscoelastic properties, but also have demonstrated potential as lubricant layers in micro-machine sensor and actuator devices. The combination of a non-destructive experimental probe and realistic simulations using accurate molecular potentials has enabled us to predict and verify the individual effects of molecular structure, intermolecular bonding, two-dimensional order, and defects on the mechanics of a lubricating film. An understanding of how the variations in microscopic structure and bonding are manifested in macroscopic film performance is essential for successful film engineering at sub-micron dimensions. Most importantly, our combination of atomic-scale viscoelastic measurements and molecular dynamics simulations provides a new opportunity to understand a wide variety of materials phenomena, including the interfacial wetting, flow and creep of technologically relevant metal and ceramic systems.

Performers: N. D. Shinn and T. A. Michalske (Sandia National Laboratories/NM), U. Landman (Georgia Institute of Technology).

Visible Photoluminescence from Metallic Nanoclusters

KC 02 03 03

Scientific Accomplishment

We have discovered that small nanometer-size metal clusters exhibit relatively intense visible, room temperature photoluminescence (PL), a completely unexpected result. Visible room-temperature PL is commonly observed from semiconductor nanoclusters and is generally shifted to considerably higher energies compared to bulk materials due to quantum size confinement of the electron-hole pairs. To our knowledge such PL has not been observed from metal nanoclusters before.

We have grown a variety of metal nanoclusters using our patented inverse-micellar synthesis approach and purified and size-selected these clusters using high pressure liquid chromatography. In earlier work we demonstrated that nanosize clusters of metals such as gold (Au) and silver (Ag) exhibit unusual optical properties such as variations in the plasmon peak frequency and width with cluster size which are not predicted by Mie theory. We have now discovered that sufficiently small clusters of these metals photoluminesce in the visible part of the spectrum. Specifically, we have found that as-synthesized Au nanoclusters, of $\approx$ 5 nm diameter or smaller, in solution, have an orange color and exhibit intense PL peaked at ~ 400 nm. A subpopulation of larger (15 nm diameter) clusters are red and do not luminesce. However, etching these larger clusters using KCN yield smaller clusters which had significant PL.

Significance — Our observations of a strong PL from metal nanoparticles may have technological applications in light emitting and sensing devices. Additionally, this discovery may provide a new approach for studying the band structure of nanosize metal particles. Comparison of the strength of the PL from the d = 5 nm clusters with that of standard dyes showed that the PL efficiency was relatively high ~10^{-4}. Previous work on rough metal films of Au had demonstrated PL but with only an efficiency of ~10^{-10}. This huge increase in the PL efficiency for small metal clusters is analogous to well-known observation of surface enhanced Raman signals from organic molecules adsorbed on small metal particle aggregates. Since the PL is so sensitive to metal interface structure, it may provide a new technique to investigate such structure.

Performers: J. P. Wilcoxon and J. E. Martin (Sandia National Laboratories/NM), F. Parsapour and D. F. Kelley (Colorado State University).

Structure and Dynamics of Inorganic Glasses

KC 02 01 01

Significant Accomplishments

New NMR tools and Raman spectroscopy indicate that a phosphate glass network remains intact when the glass is heated hundreds of degrees beyond the glass transition temperature, Tg, whereas alkali ions controlling conductivity are mobile even below Tg. This result explains why macroscopic phenomena like viscous flow are controlled by the network until it ruptures at very high temperature. Unexplained features in heat capacities and structural relaxation times of mixed alkali phosphate glasses appear to represent universal behavior controlled by the coupling of network and ion dynamics near Tg.

Our studies of alkali phosphate glasses, including dielectric and mechanical relaxation measurements and Brillouin and NMR spectroscopies, reveal two, general, temperature-dependent relaxation modes: those that involve alkali ions and those that involve the phosphate network. In glass melts, well above Tg, these modes have comparable relaxation rates. As Tg is approached upon cooling, the alkali modes are decoupled from those of the phosphate chain, occurring many orders of magnitude faster as the glass is cooled to room temperature. Similar dynamic processes are responsible for the 'anomalies' in the specific heat and structural relaxation times in mixed alkali metaphosphate glasses. These phenomena are related to changes in the Adam-Gibbs configurational entropy of the system, which is a microscopic view in which the alkali ions occupy distinct structural environments that cause coupling to network relaxations when the system approaches Tg. These effects are anticipated to be universal for glass melts.

Significance — Our results indicate that the microscopic processes that control macroscopic dynamic properties of phosphate glasses are significantly different from those of more cross-linked silicate glasses. Understanding these properties requires detailed information about glass structure, above and below Tg, and its relationship to a variety of relaxation phenomena. The development of new multi-dimensional and multiple-quantum NMR tools is important to this understanding and will have far-reaching consequences for glass science by providing a new level of quantitative structural information. For example, the apparent anomalies in the heat capacities and structural relaxation times of mixed alkali phosphate glasses appear to represent universal behavior controlled by the coupling of network and ion dynamics near Tg.

Performers: R. K. Brow, T. M. Alam, and D. R. Tallant (Sandia National Laboratories/NM); P. F. Green, (University of Texas).

Huge Seebeck Coefficient Enhancement in Boron Carbides: Vibrational Contribution to the Seebeck Coefficient of Polaronic Carriers

KC 02 02 05

Scientific Achievement

We have demonstrated and explained the unprecedented occurrence of very large Seebeck coefficients in solids having high carrier densities. The Seebeck coefficient is the emf generated across a material in response to an applied temperature differential. Alternatively stated, the Seebeck coefficient is the entropy transported by a charge carrier per carrier charge. In conventional solids the Seebeck coefficient is only large when the carrier density is small. Our prior measurements on boron carbides directly reveal high densities of low-mobility carriers that move by thermally assisted polaronic hopping. Our new measurements show that boron carbides' Seebeck coefficients are very much (about 100 times) larger than expected. Furthermore, the temperature dependence of boron carbides' Seebeck coefficients is quite unusual. We have shown that the huge Seebeck coefficients and their distinctive temperature dependence are expected from hopping-type polarons that soften the bonds surrounding them.

Significance — Thermoelectric devices provide a purely electronic means of cooling. Thermoelectric devices also generate electric power from sources of heat. These devices are used to obtain power from waste heat and to generate power in remote locations. This work demonstrates a novel means of producing especially efficient thermoelectric devices. In particular, our experiments demonstrate that large Seebeck coefficients can coexist with high carrier densities. Our explanation of this novel effect indicates that the effect will occur in other materials in which polaronic carriers soften their environment. We are now searching for large Seebeck coefficients in other materials in which carriers are confined to small atomic cages, e.g., clathrates.

Performers: T. L. Aselage, David Emin, (Sandia National Laboratories/NM), and S. S. McCready, (University of New Mexico)

Strong Influence of Morphological Defects on Nanomechanical Properties

KC 02 01 02

Technical Achievement

We have used the Interfacial Force Microscope (IFM) to study the nanomechanical properties of carefully prepared, single-crystal Au(111) surfaces and discovered a strong influence of step edges on the stress threshold for plastic deformation. The sample was prepared by sputter annealing in a UHV Scanning Tunneling Microscopy system until the standard "herring bone" reconstruction was observed. After cleaning, the sample was immersed in an alkanethiol solution for the IFM work. The self-assembling thiol monolayers passivate the normally strong adhesive interaction between our 25 nm W probe and the Au surface and IFM images show large, atomically smooth terraces intersected by single- and double-atomic steps located along crystallographic directions. By performing IFM nanoindentation at various distances from the edges of these steps, resulting in the displacement of only a few thousand Au atoms, we have shown that the shear stress at the plastic threshold is very sensitive to the presence of atomic-level surface defects. The threshold stress value is found to be almost a factor of two lower when the indentation straddles a step edge compared to when it is on a terrace several thousand Å away from any step edges. This indicates that the step edge facilitates the nucleation of dislocations and encourages plasticity at lower stress values. In addition, we find that when the indentation is near a step edge, the edge itself is attracted to the dent--retracting or extending depending on whether the indentation is on the upper or lower neighboring terrace.

Significance — These results represent the first measurements of the effect of atomic-level morphological defects on the nanomechanical properties of a material and open the study of material properties on the nanometer scale and at the most fundamental level. Although classical treatments of crystal plasticity have been used to predict the role of surface defects, our measurements provide the first direct evidence that can be used to characterize such effects. Such studies, done at various temperatures and in the presence of adsorbates and bulk impurities, will facilitate the development of models of dislocation nucleation and plastic flow and offer the potential for being able to control and tailor these important processes for specific material applications.

Performers: J. D. Kiely, J. E. Houston and T. A. Michalske (Sandia National Laboratories/NM), and R. Q. Hwang (Sandia National Laboratories/CA).

Controlled Growth of High-Quality Tl-Ba-Ca-Cu-O High-Temperature Superconducting Thin Films

KC 02 02 02

Scientific Accomplishment:

We have developed a modified crucible growth process for controlled thallination of Tl-Ba-Ca-Cu-O high-temperature superconducting (Tl-HTS) thin films. The new process allows independent control of the key variables during synthesis, the substrate temperature and the partial pressures of thallium oxide and oxygen. Both the *thermodynamics* and *kinetics* of growth must be taken into account to produce Tl-HTS films with a single structural phase and optimized superconducting properties such as critical current density. The volatility of thallium oxide at the growth temperatures makes single-phase growth difficult and the modified crucible process solves this problem.

Growth of high-quality, single-phase Tl-HTS thin films on $LaAlO_3(100)$ substrates proceeds via a two-step process. An amorphous Ba-Ca-Cu-O thin film precursor is sputter deposited onto the substrate. The precursor film then undergoes a high-temperature thallination anneal under a specified oxygen ambient in an alumina crucible, which also contains a Tl-Ba-Ca-Cu-O mixture that serves as a controlled source of TlO_x for the synthesis of the Tl-HTS film. By varying the substrate temperature and the partial pressures of TlO_x and O_2, we have successfully grown single-phase Tl-HTS films with each of the four major structural phases.

Significance — Superconductivity is on nearly every major critical technology list, with expectations for a revolutionary impact in electronics, energy, transportation, medical and military applications. The most promising applications for superconducting thin films are in microwave device components for radar and in communications including advanced navigation aids, cellular telephones and satellite. Tl-HTS films have the best properties for these applications. The low microwave surface resistance of Tl-HTS films enables substantial reductions in both the size and weight of these components (delay lines, phase shifters, filters, antennas, resonators and non-linear devices). Tl-HTS stripline devices, the size of a microchip, exhibit very low loss and the most promising power handling to date. Use of Tl-HTS microwave components provide an *unequaled* combination of size and performance to any competing technology, making superconducting films useful for many emerging high-power electronic device needs of DOE Defense Programs, aerospace and commercial wireless communications. The ability to reproducibly grow high quality thin films is crucial to the technological exploitation of these materials. Our new growth process is a very important step toward this end.

Performers: M. P. Siegal, E. L. Venturini, B. Morosin, D. L. Overmyer, and P. P. Newcomer (Sandia National Laboratories/NM).

First-Principles Model for Surfactant-Directed Growth on Platinum Surfaces

KC 02 02 02

Scientific Accomplishment

We have used QUEST, a massively-parallel, first-principles code, to compute the energies of oxygen atoms in various arrangements on (111)-oriented, stepped platinum surfaces. The calculations are a part of an effort to develop a scientifically-based understanding of how foreign atoms modify nucleation and growth processes and control the evolution of thin-film morphology. The system of oxygen atoms on the (111) crystal face of platinum is of particular interest because atomic-resolution STM data reveal a very definite "surfactant" effect. In this system, the presence of oxygen changes the growth mode from rough, three-dimensional island formation to a smooth, layer-by-layer process. The effect has been attributed to the promotion of interlayer transport of platinum atoms by oxygen atoms residing at the edges of growing islands. Our total-energy calculations show that oxygen atoms bind in different configurations near step edges depending on the "type" (i.e., crystallographic direction) of the step. The results account remarkably well for features identified as oxygen atoms in STM images. The source of the different bonding configurations is attributed to a competition between an energetic preference for oxygen to passivate as many platinum edge atoms as possible and a preference for the situation where there is no platinum atom lying directly below in the next atomic layer.

Significance — The ability of our first-principles code to determine precisely the location of oxygen atoms along step edges on a metal surface provides compelling evidence that our numerical modeling scheme faithfully predicts the structural energetics of very complex (low-symmetry) systems. As a result, we can now compute, with confidence, the nature and size of the energetic barrier to interlayer transport of platinum atoms at the two kinds of steps, with and without the presence of oxygen atoms. This is a very important step towards our goal of understanding the fundamental role of foreign atoms in directing thin-film growth. Just as important, the calculations are providing the necessary physical insight to understand why chemical adsorbates prefer to bind at particular sites near defects on surfaces. This insight will enable us to develop models of surfactant-mediated growth in systems for which atomic-level experimental investigations may not be feasible.

Performer: P. J. Feibelman (Sandia National Laboratories/NM).

IN-SITU Monitoring of Stress Evolution During Film Growth

KC 02 01 03

Scientific Achievement:

Accomplishment — A simple but sensitive technique has been developed for measuring the evolution of thin film stress during deposition and processing. The technique is based on creating an array of parallel laser beams from a single beam using a highly reflective optical element. This array is reflected from the thin film surface, and deflections of the beams (as measured by a CCD camera) are used to determine the curvature of the substrate, which is proportional to the film stress. The technique has been used to measure the evolution of stress during the epitaxial growth of SixGe1-x alloys on Si(001) substrates. A sensitivity of > 20 km has been demonstrated, sufficient to measure the stress from 0.1 monolayers of Ge on Si(001). Measurements of stress evolution during high temperature growth have, for the first time, determined the kinetics of stress relaxation induced by islanding on the surface. Stress measurements have also been used to measure the segregation of Ge to the surface during alloy growth with monolayer sensitivity, an order of magnitude better resolution than can be obtained using post-growth characterization.

Significance — This simple stress sensor makes it possible to monitor the real-time evolution of film stress in the actual processing environment. The multi-beam approach provides reduced sensitivity to vibration and greater ease of operation than prior techniques. The method is not limited to semiconductor materials and is applicable to deposition by sputtering, chemical vapor deposition and other techniques. In situ stress monitoring enables much more rapid process optimization than possible with ex situ characterization techniques. In addition, creation of a 2-dimensional array of parallel beams allows rapid surface profiling of the film stress that can be used to monitor process uniformity. Improved understanding of the relationship between film stress and the resulting morphology is critical for producing high-quality interfaces and optimal performance of advanced opto-electronic devices.

Performers: E. Chason and J. A. Floro (Sandia National Laboratories/NM).

Plasma Synthesis Enhances Control and Understanding of Optical-Ceramic Properties

KC 02 01 03

Scientific Accomplishment

Fundamental studies of the synthesis of alumina (Al_2O_3) and erbium-doped alumina using electron cyclotron resonance plasmas have yielded advances which extend and mechanistically illuminate the properties of optical ceramics. First, the mechanism governing the formation of the crystalline gamma phase of Al_2O_3 at low temperatures was determined. Normally, physical vapor deposition techniques form the amorphous phase at temperatures below 850°C. However, if during the deposition process, low-energy oxygen ions are extracted from a plasma with sufficient energy to cause displacement of aluminum atoms in the surface of the Al_2O_3, then the gamma phase forms at temperatures as low as 400°C. Second, a method was developed for simultaneous incorporation of optically active, rare-earth elements such as erbium (Er) into optical ceramic waveguide materials: Al_2O_3 and La_2O_3. This low temperature, plasma-assisted deposition technique enables the direct integration of optical amplifiers into compound-semiconductor photonic integrated circuits. Previously, direct integration of the optical amplifier on compound semiconductors was unattainable because the technology utilized ion implantation to incorporate Er into the optical ceramic, followed by a high temperature annealing treatment to reduce implantation damage. This damage causes a decrease in optical quality as evidenced by a decreased radiative lifetime, and high temperature annealing treatments are incompatible with compound semiconductor devices. Furthermore, by controlling the phase of the material, the local environment of the Er was manipulated in order to understand and enhance the optical activity of this ceramic system. Contrary to previous belief, the local environment of Er in gamma Al_2O_3 is more like that in amorphous Al_2O_3 than in alpha Al_2O_3 (sapphire). Erbium in the gamma phase has a significantly longer radiative lifetime than Er in sapphire, and therefore this plasma-synthesis process provides a method to form high quality optical devices.

Significance — Ceramic materials can be used across a broad spectrum of applications requiring optical signals and data transfer. These applications range from amplification of signals in long-distance communication to use in high voltage locations where electrical isolation is essential, e.g., safeguarding weapons from inadvertent electrical shock. Improvement in the optical quality and luminescence efficiency of these materials helps to enable these applications and future optical device technologies. Further, utilization of optical signals will be greatly improved in all of these applications as new methods are developed for the miniaturization and the integration of components into systems. The science and technology learned in these investigations is the first step to creating a monolithic photonic integrated circuit in which the light generation source (generally a compound semiconductor light source) is close-coupled to the amplification, waveguide, and other optical-ceramic components. In this way, both miniaturization and system integration can be achieved with the most efficient, highest quality optical materials.

Performers: J. C. Barbour, B. G. Potter, D. M. Follstaedt, J. A. Knapp, M. B. Sinclair, and C. H. Seager (Sandia National Laboratories/NM).

Reflectance Difference Spectroscopy Reveals the State of the Surface During GaAs MOCVD

KC 02 03 03

Scientific Accomplishment

We have implemented reflectance-difference spectroscopy (RDS) on a state-of-the-art III-V vertical-flow rotating-disk MOCVD reactor, and have correlated RDS spectra with surface structures/reconstructions characteristic of typical deposition conditions. In this way we have for the first time, correlated surface structures/reconstructions known from surface-science diagnostics with those present during actual MOCVD.

For example, RDS spectra taken at typical growth temperatures around 640°C indicate that the GaAs (100) surface exists in a so-called super-arsenic-rich reconstruction, characterized by a negative peak at 2.2-2.3 eV. Previously, we had conjectured that the GaAs (100) surface would exist in this reconstruction in order to explain a group-V-suppressed MOCVD growth rate measured using ultra-accurate, real-time, in-situ optical reflectance. In our model, As atoms partially occupy Ga surface lattice sites, obstruct the adsorption of gas-phase Ga-containing species, and hence suppress the overall GaAs growth rate. Our new RDS measurements are strong evidence that this arsenic site-blocking MOCVD model is correct and illustrate the power of connecting UHV and at-pressure measurements through optical diagnostics such as RDS.

Significance — These measurements are the first in which surface structures/reconstructions deduced from UHV measurements have been correlated directly and quantitatively to those deduced from at-pressure MOCVD measurements. They show the power of RDS, in conjunction with kinetic modeling, in making such correlations. In the example described here, they have provided strong confirmation for a conjectured mechanism for our recent observation of a group-V suppression of growth rate under actual MOCVD conditions. We expect this to be the first of many examples in which surface structures/reconstructions under actual MOCVD process conditions are probed using RDS and connected to surface species and reactive sites deduced from UHV measurements. These advances in understanding are expected to lead to improved properties and control in the growth of thin films.

Performers: J. R. Creighton, H. K. Moffat, and K. Baucom (Sandia National Laboratories/NM).

VII. Research Program Summaries

B. Research Summaries

Physics and Chemistry of Ceramics
KC 02 01 01

Principal Investigators: T. M. Alam, R. A. Assink, T. J. Boyle, C. J. Brinker, R. K. Brow, K. Chen, A. J. Hurd, P. R. Schunk, and R. W. Schwartz

Goals: To understand the chemical and physical processes that determine the structure and properties of ceramics and glasses and to establish a fundamental technology base for ceramics for DOE Technologies.

Recent Highlights

- Beam bending (BB) experiments directly measuring stress in complex microporous material gave results opposite in sign to classical theory. Solvation forces, described by density functional theory, explained compressive stress under solvent vapor.
- Surfactant templated mesoporous films. Surfactant self-assembly during dip-coating resulted in mesoporous films exhibiting liquid crystalline domains; optical fluorescence depolarization probed the surfactant assembly process in situ.
- Developed a synthesis of PZT powders that can be redissolved to circumvent solution aging effects. The powders are needed for the production of key material in DP neutron generator components.
- Patents filed for synthesis of two Nb compounds, $Pb(Mg,Nb)O_3$ and Nb-doped PZT. The thin-film properties of these materials have been investigated; ^{93}Nb NMR has been critical in determining solution properties of these compounds.
- Synthesis of the first crystallographically characterized titanium alkoxide, $[Ti(ONp)_4]_2$ (ONp = OCH_2CMe_3). This novel, highly soluble and volatile species was found to be di-nuclear in solid state and monomeric in solution by $^{47,49}Ti$ NMR.
- Developed a model of glass nucleation and growth that interprets precursor structural and thermal processing effects on ceramic thin film microstructure induced through the addition of a second chelating ligand to the precursor molecules.
- Entropy and distributions of particle contact forces in 2D computer simulations of polydisperse powder were found to exhibit power-law form, in light of which a stability criterion for 2D packings was examined.
- Completed two-phase model of sol-gel film drying in dip coating, incorporating a deformable porous film coupled with overlying buoyant gas flow through a unique boundary condition; confirms the importance of gas transport.
- Examined the molecular structure and time dependent relaxations in phosphate glasses above and below the glass transition to gain insight into the processes that control viscous flow, mechanical relaxation, and ionic conductivity.

Future Directions

- Porous Materials. Measurement of stresses during film deposition by beam bending, *in situ* spectroscopic ellipsometry under controlled atmosphere, and DFT will yield evolution of pore size and its polydispersity. Elucidation of the gel point during film deposition, attempted by viscoeleastic response to a jet of air (glaucoma test) and by rotational diffusion of tethered fluorescent groups aided by FTIR and AFM, may explain profound interfacial ordering effects in surfactant-templated mesoporous films. Efforts to predict stress via condensation chemistry and solvation forces will be leveraged by Coating Research Consortium studies of polymeric (organic and inorganic) films.
- Complex Precursors. Pursue fundamental understanding of nucleation, growth, and epitaxial effects in ceramic film processing by a variety of analytical and spectroscopic techniques. Our new, well-characterized titanium alkoxide precursors allow us to model the synthesis process and compare to observed transformation behavior. We'll follow the transformation pathway in metal alkoxides using ^{17}O NMR and further develop central atom NMR spectroscopy of ^{93}Nb, $^{47,49}Ti$, ^{15}N, ^{209}Bi, and ^{119}Sn. 2D NMR with ^{17}O and alternative central atom nuclei will be initiated.

- Glass Dynamics. Phosphate glasses will be the focus by measuring both the real and imaginary parts of shear moduli from room temperature through Tg and into the melt and performing ^{31}P MAS 2D Exchange NMR experiments to characterize P-tetrahedral connectivities. We will initiate 2D MQ NMR to obtain information about alkali bonding and will perform ^{17}O MAS NMR analyses to characterize oxygen bonding.

Relationship to DOE and Industial Technologies

- Stockpile Stewardship. Our ^{93}Nb and ^{17}O NMR techniques are now used to study aging and reliability of weapon materials.
- Integrated Enterprise. Personnel exchanges with Texas Instruments have enhanced the development of our novel SBT ($SrBi_2Ta_2O_9$) for optical applications. Industrial CRADA funds from a consortium of coating companies interested in sol-gel and organic thermosets leverage our effort to model polymerization by condensation in sol-gel films.

Program Quality

Brow is the first American to win the *Gottardi Prize,* from the International Commission on Glass, for work on the structure and dynamics of phosphate glasses. **Brinker** was awarded a patent for low temperature/pressure aerogels, which promptly won him an *R&D100 Award* and the *Lockheed-Martin Corporate NOVA Award.* **Cairncross** won the *Outstanding Young Investigator Award* from DOE/DP ***and*** the *Presidential Young Investigator Award*, while **Hurd** was elected *Treasurer* of the MRS and *Chairman* of the LANSCE User Group. Over 12 invited talks, 2 invited review papers, 2 invited papers, 18 papers, 1 patent.

Publications

1. AMORPHOUS SILICA MOLECULAR SIEVES BY SOL-GEL PROCESSING, G.Z. Cao, Y.F. Lu, L. Delattre, C.J. Brinker, and G.P. Lopez,, Adv. Mater., 8 (1996) 588-591.
2. CHEMICAL SENOSRS BASED ON HYDROPHOBIC POROUS SOL-GEL FILMS AND ATR-FTIR SPECTROSCOPY, Y. Lu, L. Han, C.J. Brinker, T.M. Niemczyk, and G.P. Lopez, Sensors and Actuators B **35**, (1996) 1-5.
3. TEMPLATE-BASED APPROACHES TO THE PREPARATION OF AMORPHOUS NANOPOROUS SILICAS, N.K. Raman, M.T. Anderson, and C.J. Brinker, Chem. Mater. 8 (1996) 1682-1701.
4. POROUS INORGANIC MATERIALS, C.J. Brinker, Curr. Opinion in Solid State and Mater. Sci., 1 (1996) 798-805.
5. PREPARATION OF MICROPOROUS FILMS WITH SUB-NANOMETER PORES AND THEIR CHARACTERIZATION USING STRESS AND FTIR MEASUREMENTS, J. Samuel, A.J. Hurd, F. van Swol, L.J. Douglas Frink, C.J. Brinker, S.C. Contakes, Mater. Res. Soc. Symp. Proc. **431** (1996) 185-190.
6. CONTROLLING THE POROSITY OF MICROPOROUS SILICA BY SOL-GEL PRCESSING USING AN ORGANIC TEMPLATE APPROACH, Y. Lu, G.Z. Cao, R.P. Kale, L. Delattre, C.J. Brinker, G.P. Lopez, Mat. Res. Soc. Symp. Proc. **435** (1996) 271-275.
7. SHRINKAGE AND MICROSTRUCTURAL DEVELOPMENT DURING DRYING OF ORGANICALLY MODIFIED SILICA XEROGELS, N.K. Raman, S. Wallace, and C.J. Brinker, Mat. Res. Soc. Symp. Proc. **435** (1996) 357-362.
8. IDENTIFICATION OF SELF- AND CROSS-CONDENSATION PRODUCTS IN ORGANICALLY MODIFIED SILICA SOLS BY 29SI AND 17O NMR SPECTROSCOPY S. Prabakar, R. A. Assink, N. K. Raman, S. A. Myers, C. J. Brinker, J. Non-Cryst. Solids 1996, **202**, 53.

9. CROSS-CONDENSATION KINETICS OF ORGANICALLY MODIFIED SILICA SOLS, S. Prabakar and R. A. Assink in Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials, ed. B. K. Coltrain, C. Sanchez, D. W. Schaefer and G. L. Wilkes (Materials Research Society, Pittsburgh, PA, 1996) p. 345.
10. IDENTIFICATION AND CHARACTERIZATION OF THE HYDROLYSIS PRODUCTS IN TMOS AND MTMS MONOMERS USING 29SI NMR AND POLARIZATION TRANSFER TECHNIQUES, T. M. Alam, R. A. Assink, S. Prabakar, and D. A. Loy , Magn. Reson. Chem. 1996, **34**, 603.
11. HYDROLYSIS AND ESTERIFICATION IN ORGANICALLY MODIFIED ALKOXYSILANES: A 29SI NMR INVESTIGATION OF METHYLTRIMETHOXYSILANE, T. M. Alam, R. A. Assink, and D. A. Loy Chem. Materials 1996, **8**, 2366.
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13. THEORETICAL MODEL FOR COMPACTION OF GRANULAR MATERIALS, V.M. Kenkre, M.R. Endicott, S.J. Glass, and A.J. Hurd, J. Am. Ceram. Soc. **79**, 3045-54 (1996).
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Work Performed Jointly with Other Programs

15. A QUALITATIVE MODEL FOR THE FATIGUE-FREE BEHAVIOR OF SrBi2Ta2O9, H. N. Al-Shareef, D. B. Dimos, T. J. Boyle, W. L. Warren, and B. A. Tuttle Applied Physics Letters 1996, **68**, 690.
16. FORMATION OF SrBi2Ta2O9, PART 2. EVIDENCE OF A BISMUTH DEFICIENT PYROCHLORE PHASE, M. A. Rodriguez, T. J. Boyle, C. D. Buchheit, B. A. Hernandez, B. Scott, J. Mat. Res. 1996, **11**, 2282.
17. FORMATION OF SrBi2Ta2O9, PART 1. SYNTHESIS AND CHARACTERIZATION OF A NOVEL 'SOL-GEL' SOLUTION FOR PRODUCTION OF FERROELECTRIC SBT THIN FILMS, T. J. Boyle, C. D. Buchheit, M. A. Rodriguez, H. N. Al-Shareef, B. A. Hernandez, B. Scott J. Mat. Res. 1996, **11**, 2274.
18. MICROSTRUCTURAL DEVELOPMENT IN SOL-GEL DERIVED PZT THIN FILMS: THE ROLE OF PRECURSOR STOICHIOMETRY AND PROCESSING ENVIRONMENT, M. J. Lefevre, J. S. Speck, R. W. Schwartz, D. Dimos, and S. J. Lockwood, J. Mater. Res. 1996,**11**, 2076.
19. SOLUTION DEPOSITION OF FERROELECTRIC THIN FILMS, B. A. Tuttle and R. W. Schwartz, Mater. Res. Bull. 1996 **21**, 49. (Invited)
20. ALCOHOL-ALKOXIDE EXCHANGE BETWEEN Sn(OBut)4 and HOBut IN COORDINATING AND NON-COORDINATING SOLVENTS, J. Caruso, T. M. Alam, M. J. Hampden-Smith, A. L. Rheingold, G. A. P. Yap J. Chem. Soc., Dalton Trans. 1996, **13**, 2659.

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1. PREPARATION OF HIGH POROSITY XEROGELS BY CHEMICAL SURFACE MODIFICATION, R. Deshpande, D. M. Smith, and C. J. Brinker, U.S. Patent No. 5565142, issued October 15, 1996.

Atomic-Level Science of Adhesion
KC 02 01 02

Principal Investigators: T. A. Michalske, J. E. Houston, N. D. Shinn, and P. J. Feibelman

Goal: To understand in atomic detail the nature of the chemical and physical interactions that control adhesive bonding and to use this understanding to: 1) develop predictive models for adhesive bond strength and stability and 2) tailor material surfaces and interfaces for optimized adhesion and lubrication properties.

Recent Highlights

- The First Measurements of the Effect of Atomic-Level Defects on Nanomechanical Properties-We have used the IFM to study the nanomechanical properties of carefully prepared, single-crystal Au(111) surfaces. By indenting at various distances from single and double steps on this surface, we have shown that the plastic threshold shear stress is lower by almost a factor of two when the indentation straddles a step edge relative to when it is a thousand Å away. These results represent the first demonstration of the effect of atomic-level defects on the nucleation of dislocations in an otherwise perfect lattice.
- Nanometer-Scale Mapping of Thin-Film Residual Stress - In earlier work IFM/nanoindentation measurements on thin Au films deposited on various substrates we demonstrated that the variation in the measured nanoindentation response can be correlated with the sign and magnitude of the residual film stress. This year we completed preliminary measurements correlating nanoindentation properties with externally applied film stress. These results strengthen our conclusion that IFM nanoindentation can be used to map thin-film stress with nanometer-scale spatial resolution. This development has significant implications for microelectronics where the ability to monitor and control residual stress in spatially patterned thin films is critical to eliminating deleterious processes such as delamination and stress voiding of IC interconnects.
- Friedel Oscillations in the Force Constants of Metals- The application of first-principles methods to predict fracture and adhesion at metal interfaces requires analytic expressions for the long-range falloff of the force constants of nearly-free-electron metals. Comparison with exact results showed that Friedel oscillations dominate the force constants of fcc Al beyond the fourth neighbor shell. We will apply this first-principles derived long-range force interaction to improve embedding theory of defect-related strain and to improve methods for determining force-constants empirically.
- Ultra-High Vacuum/IFM System - The newly completed UHV/IFM has been applied to studies of clean Au surfaces. This is the first time that such measurements have been made in the absence of the usual sensor jump-to-contact. The results provide critical information concerning the formation of the adhesive bond solely under the influence of the interfacial interaction, including the role of surface morphology, roughness and the presence of adsorbates, as well as the elastic and plastic response of the material itself. The same information is available concerning the failure of the adhesive bond as the surfaces are separated. These data clearly demonstrates the role of surface energy-driven wetting and self-diffusion in the formation and stability of metal-metal adhesive bonds.

Future Directions

The program will continue to focus on nanometer-scale measurements of interfacial adhesion and the development of theoretical models to address the chemical stability of the adhesive bond. The probe tips and substrate surfaces will be tailored with self-assembled monolayer films to controllably examine the role of surface chemical groups on the formation and stability of the adhesive bond. With the UHV/Surface Science IFM in operation, adhesion events will be examined on clean and adsorbate covered surfaces and the results compared with first principles atomistic simulations. We will also use the IFM to probe the mechanical response of small-scale structures so that we can better understand the behavior of materials near stress singularities and of nanoscale composite materials. We will also begin finite element and atomistic modeling to interpret nanoindentation results.

Interactions with DOE Technologies:

Our fundamental studies of interfacial adhesion increase the reliability of composite materials interfaces that are important to DP funded R&D and the Materials Joining Project of the DOE Synthesis and Processing Center.

Program Quality

11 publications, 7 invited presentations (MRS, TMS, ACS, AVS, Adhesion Society, Canadian Chem. Soc.)

Publications

1. DISLOCATION NUCLEATION AT NANOSCALE CONTACTS, T. A. Michalske and J. E. Houston, Acta. Met. (In Press).
2. INTERFACIAL ADHESION AT THE MOLECULAR LEVEL, J. E. Houston, T. A. Michalske and R. M. Crooks, Proc. Adh. Soc. (In Press)
3. THE EFFECT OF STRESS ON THE NANOMECHANICAL PROPERTIES OF AU SURFACES, J. E. Houston, Proc. MRS Symposium, Fall 1996 (In Press).
4. NEAR-PLASTIC THRESHOLD INDENTATION AND THE RESIDUAL STRESS IN THIN FILMS, J. E. Houston and T. A. Michalske, Proc. MRS, Symposium, Spring 1996 (In Press).
5. THE EFFECT OF PROBE RADIUS ON THE THRESHOLD SHEAR STRESS FOR THE SINGLE-CRYSTAL Au(111) SURFACE, J. E. Houston, T. A. Michalske, P. Tangjunyong, J. Mat. Res. (In Press).
6. THE DIRECT OBSERVATION OF INTER-GROUP BONDING USING INTERFACIAL FORCE MICROSCOPY, R. M. Crooks, R. C. Thomas, J. E. Houston, T. Kim and T. A. Michalske, J. Adhesion Soc. (In Press).
7. ADSORPTION AND THERMAL STABILITY OF Mn ON TiO2(110); X-RAY ABSORPTION SPECTROSCOPY AND X-RAY PHOTOEMISSION, U. Diebold and N. D. Shinn, Phys. Rev. B (In Press).
8. FRIEDEL OSCILLATIONS IN THE FORCE CONSTANTS OF METALS, Phys.Rev. B (In Press).
9. WAFER LEVEL THIN-FILM SOLDER BONDING OF A HYBRID SENSOR FOR INTERFACIAL FORCE MICROSCOPY, C. M. Matske and J. E. Houston, Proc. SPIE International Symposium, Spring 1997 (In Press).
10. TOWARDS AN UNDERSTANDING OF LIQUID METAL EMBRITTLEMENT: ENERGETICS OF Ga ON Al SURFACES, R. Stumpf and P. J. Feibelman, Phys. Rev. B54, 5145(1996).
11. NANOMECHANICAL BASIS FOR IMAGING SOFT MATERIALS WITH TAPPING MODE ATOMIC-FORCE MICROSCOPY, A. J. Howard, R. R. Rye and J. E. Houston, J. Appl. Phys. 79, 1885 (1995).

Wetting And Flow of Liquid Metals and Amorphous Ceramics At Solid Interfaces
KC 02 01 02

Principal Investigators: N. D. Shinn, T. A. Michalske (Sandia National Laboratories/NM), U. Landman (Georgia Tech.), F. G. Yost, and R. Cannon (LBNL)

Goal: To experimentally measure and theoretically model the atomic-scale processes that control fluid flow near solid interfaces and use these understandings to develop predictive models for macroscopic wetting and flow behavior.

Recent Highlights:

- Liquid Metal Melting - We have made the first viscoelastic measurements of melting and solidification in ultra-thin liquid metal layers using our newly developed Acoustic Wave Damping (AWD) technique. We observe melting and metastable undercooling — by as much as 30°C — for 10-50nm thick indium layers evaporated onto tantalum or chromium electrodes of a quartz crystal microbalance sensor in ultra-high vacuum. Our frequency spectrum analysis approach enables us to unambiguously distinguish indium phase changes from thermal stress effects in the sensor. These results clearly demonstrate the ability of our new experimental approach to quantify the unique thermal/physical properties of thin interfacial wetting layers and point to significant differences in thin layer properties that can dramatically impact the formation and stability of joined interfaces.
- Monolayer Shear Response - Self-assembled monolayers (SAMs) are not only good model systems for studying the relationship between atomic-scale structure and interfacial viscoelastic properties, but also are effective lubricant layers in micro-machine sensor and actuator devices. For alkane-thiol SAMs, the elastic shear modulus increases with chain length, from ~0.01 MPa (C_{12}) to ~0.1 MPa (C_{18}). Short chain SAMs exhibit an apparent modulus increase with shear rate not seen for longer alkane SAMs, reflecting the loose molecular packing within short-chain monolayers. These findings suggest the ability to tailor a monolayer's mechanical properties by the selection of its constituent molecules.
- Mechanistic Insights Into Viscoelasticity - Molecular dynamics simulations of model systems enable the viscoelastic properties measured by AWD to be related to atomic scale bonding and structure. Using realistic potentials, simulations have been performed for a perfectly ordered monolayer of C_{16} alkane thiol molecules on Au(111). By applying a static shear stress to the SAM, a theoretical elastic modulus of >10MPa is calculated, which exceeds experimental values. However, inertially shearing the SAM by a high-frequency lateral translation of the gold substrate (analogous to the AWD experiment) reveals that the ensemble response involves azimuthal molecular rotation about the surface normal, rather than the expected molecular libration. This unexpected quasi-rotational motion is energetically preferable to one-dimensional shear and can account for the lower measured elastic modulus. Very recent simulations further show that the introduction of defects into the SAM leads to energy dissipation that is absent in the perfectly ordered monolayer. This illustrates how realistic simulations and AWD experiments enable us to predict and verify the individual effects of molecular structure, intermolecular bonding, order, and impurity incorporation on the mechanics of real films.

Future Directions:

In the initial phase of this program we have established Acoustic Wave Damping (AWD) as a viable technique for measuring the viscoelastic properties of thin layers. We coupled AWD experiments with molecular dynamics simulations to understand the viscoelastic shear response of model molecular layers, then progressed to elevated temperature experiments. We will further develop new high-temperature AWD technologies (cw and pulsed) while incorporating complementary spectroscopic interface characterization tools for metal and ceramic flow studies. Our nanoscale studies will include melting, undercooling and viscosity measurements of non-reactive liquid metals as a function of thickness, interface morphology and chemical composition. This will be followed by chemically reactive metals, atomically diffuse interfaces, and ceramic films. We will use the microscopic results to derive new models to predict complex

macroscopic spreading and creep behavior. This systematic progression through increasingly complex but well-defined interfacial structures will enable us to evaluate the role of various energy dissipation mechanisms, interface morphology, impurities, surfactants, and chemical reactions in determining macroscopically observed wetting, spreading, and creep behavior.

Interactions with DOE Technologies:

Improving the wetting behavior of liquid metal alloys will greatly increase the reliability of widely used joining technologies such as soldering and brazing. This BES work is providing a scientifically sound understanding of the atomistic flow processes that control solder wetting and flow for high-reliability defense microelectronics applications. This program will establish interactions with DP-funded R&D and with the Materials Joining Project of the DOE Synthesis and Processing Center.

Program Quality: 3 publications

Publications

1. WETTING KINETICS IN SURFACE CAPILLARY GROOVES, R. R. Rye, F. G. Yost, and J. A. Mann, Jr., Langmuir **12**, 4625 (1996).
2. SOLDER WETTING KINETICS IN NARROW V-GROOVES, F. G. Yost, R. R. Rye, and J. A. Mann, Jr., Acta Materialia (in press).
3. VISCOELASTIC RESPONSE OF SELF-ASSEMBLED ALKANE-THIOL MONOLAYERS TO SHEAR, N. D. Shinn, T. A. Michalske, C. Daly, R. Limary and U. Landman, Langmuir (submitted).

Energetic Particle Synthesis and the Science of Materials
KC 02 01 03

Principal Investigators: J. C. Barbour, M. T. Dugger, D. M. Follstaedt, J. A. Knapp, S. M. Myers, C. H. Seager and W. R. Wampler

Goals: Use energetic beams and plasmas to create superior new materials and achieve fundamental understanding of the atomic processes and microstructures that govern materials synthesis and properties.

Research Highlights

- ECR-plasma growth of Er-doped Al_2O_3. Using electron-cyclotron-resonance (ECR) plasmas, we grew Al_2O_3 films containing optically active Er with long radiative lifetimes. In contrast to present Er doping by ion implantation, this breakthrough enables low-temperature processing, unrestricted film thickness, and phase selection between γ and amorphous Al_2O_3 by adjustment of plasma-particle energy and substrate temperature.
- Finite-element modeling of nanoindentation. Our further development of this modeling established the capability to quantify by diamond-tip nanoindentation the intrinsic elastic and plastic properties of submicrometer films with a reliability approaching that of macroscopic tensile testing. Applications of the method encompassed intrinsic layer hardnesses from 0.1 GPa (Al) to 70 GPa (diamond-like carbon) and layer-to-substrate hardness ratios above 10 (Al-Al_2O_3 on Al and amorphous Ni-Ti-C on Ni).
- Strength of amorphous Ni-Fe layers stabilized by Ti+C. Amorphous $Ni_{68}Ti_{16}C_{16}$ formed on Ni by ion implantation, and amorphous $Fe_{64}Ti_{18}C_{18}$ formed on Si by pulsed laser deposition (PLD), were shown by nanoindentation to have very high strengths, with yield stresses near 5 GPa and intrinsic hardnesses of about 15 GPa. These values were quantitatively understood as arising from Ti-C pairing and the absence of mobile dislocations. Such high strengths illuminate the favorable tribological characteristics of this class of alloys.
- Strong gettering of transition metals by B-Si precipitates in Si. We discovered and quantitatively characterized strong gettering of transition-metal impurities by B-Si precipitates in Si. Studies of Fe, Co, Cu, and Au solutes indicated that the B-Si phase, a structurally disordered precursor of icosahedral B_3Si formed by B implantation, getters by exothermic segregation of metal atoms from solution in the Si phase to solution in the B-Si.
- Energetics of Cu on (111) and (100) Si surfaces. We determined the relative stabilities of the principal Cu states on Si surfaces for the first time, thereby elucidating cavity gettering. In UHV experiments on LEED-characterized external surfaces, ion-beam analysis measured diffusion-mediated equilibrium between the surface and internal, implantation-formed Cu_3Si. In stability, Cu(5×5)/Si(111) > Cu_3Si > Cu(2×1)/Si(100).
- BES S&P Center - Hard-layers. Our quantification of the strength and elastic modulus of diamond-like carbon films synthesized at LBNL was central to the continuing development of these hard (~70 GPa) and tribologically superior materials. We also provided essential compositional analysis in the development of hard BN, BC, and B suboxide films at SNL-CA and ORNL using our advanced capability for high-energy elastic recoil detection.
- Relevance to DOE Defense Programs. Hard layers developed in this program are expected to enhance the performance and lifetime of micro-electromechanical systems in defense applications.

Future Directions

- Synthesis of superior new materials using energetic beams and plasmas
  - High-strength Al, Fe, Ni and Au-based nanoalloys formed using ion implantation, PLD, and ECR plasmas.
  - Implanted layers in Si and compound semiconductors for gettering and defect trapping.

- Oxides and nitrides grown from ECR plasmas for surface passivation, optical structures, and hard layers.

- Ion-beam studies of fundamental atomic processes, defects, and microstructures
  - Trapping mechanisms for detrimental impurities and defects in semiconductors.
  - Hardening mechanisms and dislocation motion in Al, Fe, Ni and Au nanoalloys.
  - Injection and reactions of H in semiconductors as related to passivation of defects, surfaces, and impurities.

Program Quality

- Eighteen publications and three invited papers in 1996.
- 1996 Inter. Conf. on Ion-Beam Modif. of Materials organized jointly by SNL (J. C. Barbour, Chair) and LANL.

Publications

1. EVALUATING MECHANICAL PROPERTIES OF THIN LAYERS USING NANOINDENTATION AND FINITE-ELEMENT MODELING: IMPLANTED METALS AND DEPOSITED LAYERS (INVITED PAPER), J. A. Knapp, D. M. Follstaedt, J. C. Barbour, S. M. Myers, J. W. Ager, O. R. Monteiro, and I. G. Brown, Proc. 1996 MRS Fall Meeting, in press.
2. FINITE-ELEMENT MODELING OF NANOINDENTATION FOR DETERMINING THE MECHANICAL PROPERTIES OF IMPLANTED LAYERS AND THIN FILMS, J. A. Knapp, D. M. Follstaedt, J. C. Barbour, and S. M. Myers, Nucl. Instrum. Meth. B, in press.
3. HARDENING OF NICKEL ALLOYS BY ION IMPLANTATION OF TITANIUM AND CARBON, S. M. Myers, D. M. Follstaedt, J. A. Knapp, and T. R. Christenson, Proc. 1996 MRS Fall Meeting, in press.
4. PARTICLE-BEAM SYNTHESIS OF NANOCOMPOSITE Al ALLOYS, D. M. Follstaedt, J. A. Knapp, S. M. Myers, and J. C. Barbour, Proc. 1996 MRS Fall Meeting, in press.
5. STRONG SEGREGATION GETTERING OF TRANSITION METALS BY IMPLANTATION-FORMED CAVITIES AND BORON-SILICIDE PRECIPITATES IN SILICON (Invited Paper), S. M. Myers, G. A. Petersen, D. M. Follstaedt, T. J. Headley, J. R. Michael, and C. H. Seager, Nucl. Instrum. Meth. B, 1996, in press.
6. BINDING OF COBALT AND IRON TO CAVITIES IN SILICON, S. M. Myers, G. A. Petersen, and C. H. Seager, J. Appl. Phys. **80**, 3717 (1996).
7. METAL GETTERING BY BORON-SILICIDE PRECIPITATES IN BORON-IMPLANTED SILICON, S. M. Myers, G. A. Petersen, T. J. Headley, J. R. Michael, T. L. Aselage, and C. H. Seager, Nucl. Instrum. Meth. B, in press.
8. GETTERING OF TRANSITION METALS BY CAVITIES IN SILICON FORMED BY HELIUM ION IMPLANTATION, G. A. Petersen, S. M. Myers, and D. M. Follstaedt, Nucl. Instrum. Meth. B, in press.
9. SEGREGATION OF COPPER TO (100) AND (111) SILICON SURFACES IN EQUILIBRIUM WITH INTERNAL Cu_3Si PRECIPITATES, W. R. Wampler, Proc. 1996 MRS Fall Meeting, in press.
10. Er-DOPED AMORPHOUS AND CRYSTALLINE Al_2O_3 AND La_2O_3 FILMS GROWN WITH LOW-ENERGY IONS FROM AN ECR PLASMA, J. C. Barbour, B. G. Potter, D. M. Follstaedt, J. A. Knapp, and M. B. Sinclair, Proc. 1996 MRS Fall Meeting, in press.

11. TRANSMISSION ION CHANNELING STUDIES OF THE SILICON (111) MONOHYDRIDE SURFACE, W. R. Wampler, Phys. Rev. B, in press.
12. UNSTABLE DISPLACEMENT DEFECTS AND HYDROGEN TRAPPING IN GaAs, H. J. Stein and J. C. Barbour, Phys. Rev. B, submitted.

Work Performed Jointly with Other Programs

1. GROWTH AND MECHANICAL AND TRIBOLOGICAL CHARACTERIZATION OF MULTI-LAYER HARD CARBON FILMS, J. Ager, O. Monteiro, I. Brown, J. A. Knapp, D. M. Follstaedt, M. Nastasi, K. C. Walter, and C. J. Maggiore, Proc. 1996 MRS Fall Meeting, in press.
2. CAVITY-DISLOCATION INTERACTIONS IN Si-Ge AND IMPLICATIONS FOR HETEROSTRUCTURE RELAXATION, D. M. Follstaedt, S. M. Myers, and S. R. Lee, Appl. Phys. Lett. **69**, 2059 (1996).
3. INTERACTION OF CAVITIES WITH MISFIT DISLOCATIONS IN SiGe/Si HETEROSTRUCTURES, D. M. Follstaedt, S. M. Myers, J. A. Floro, and S. R. Lee, Nucl. Instrum. Meth. B, in press.
4. INTERACTION OF CAVITIES AND DISLOCATIONS IN Si-Ge, D. M. Follstaedt, S. M. Myers, and S. R. Lee, Proc. 1996 MRS Fall Meeting, in press.
5. COMPETITIVE GETTERING OF COPPER IN CZOCHRALSKI SILICON BY IMPLANTATION-INDUCED CAVITIES AND INTERNAL GETTERING SITES, S. A. McHugo, E. R. Weber, S. M. Myers, and G. A. Petersen, Appl. Phys. Lett. **69**, 3060 (1996).
6. COMPETITION BETWEEN GETTERING BY IMPLANTATION-INDUCED CAVITIES IN SILICON AND INTERNAL GETTERING ASSOCIATED WITH SiO_2 PRECIPITATION, S. A. McHugo, E. R. Weber, S. M. Myers, and G. A. Petersen, Proc. 1996 MRS Fall Meeting, in press.

Advanced Growth Techniques And The Science Of Epitaxy
KC 02 01 03

Principal Investigators: E. Chason, J. A. Floro, J. Han, B. S. Swartzentruber, R. Q. Hwang, J. Y. Tsao, W. B. Gauster

Goals: To develop advanced growth techniques and in situ diagnostics for fundamental understanding of the science of epitaxy and thin film growth.

Recent Highlights

- Strain Relaxation from Morphological Instabilities during SiGe Heteroepitaxy - Using our new multi-beam optical stress monitoring technique, we have obtained the first measurements of the kinetics of stress relaxation induced by morphological changes such as islanding or rippling. The onset of stress relaxation occurs coincidentally with a rapid increase in the surface roughness as determined by reflection high energy electron diffraction (RHEED). The stress relaxation is in reasonable agreement with preliminary finite element calculations based on post-growth measurements of the surface morphology using atomic force microscopy and transmission electron microscopy. Although it has been suggested previously that films can relieve their stress by morphological changes, there have been no quantitative measurements of the magnitude of the stress relief.
- Measurement of Surface Segregation during Heteroepitaxial Growth - In situ stress monitoring has been used to measure the segregation of Ge to the surface during SiGe growth on Si(001). These measurements have made it possible to characterize the composition profile with monolayer sensitivity, an order of magnitude greater than can be obtained with ex situ techniques. Interface control with this level of sensitivity is critical for achieving optimal performance in short-period strained layer structures.
- Biaxial Modulus of Strained SiGe Films - Using the optical stress monitor, we have measured the elastic modulus of biaxially-strained SiGe films. These measurements indicate that a simple rule of mixtures can be used for film strains up to 2.4% before the effects of higher order elastic constants become important. This techniques enables the measurement of elastic constants at much larger strains than can be obtained by other methods.
- Si Monomer Trapping at Steps and Islands on Si(001) - Using variable temperature STM, we discovered that during growth single Si atoms can become trapped at the ends of dimer rows along steps and island edges. The large binding energy of atoms in these sites facilitates the epitaxial growth of the crystal lattice along preferred directions because the atoms are more likely to encounter others in these highly reactive lattice sites.
- Development of Optical-Probe-Compatible GaN MOCVD Reactor -- (Joint with LDRD) We have developed a high-temperature high-speed rotating-disk MOCVD reactor and demonstrated growth of high-structural-quality GaN materials. The real-time optical stress monitoring technique is being implemented on this system to study the effect of CVD growth parameters on the nucleation rate, growth rate and residual stress.

Future Directions

Controlling stress and morphology are critical for many advanced applications of thin films. We will use our advanced in situ diagnostics to measure the evolution of film stress and surface morphology to better understand the origin of morphological instabilities. Understanding the kinetics of Ge surface segregation will enable us to understand the interaction of surface stress and film composition in order to produce heteroepitaxial structures with sharper interfaces. STM studies of SiGe heteroepitaxy will identify the atomistic mechanisms associated with SiGe growth and the compositional segregation. We will combine our techniques for measurement of surface structure (X-rays, scanning probe microscopy) and film stress (optical stress sensor) to develop a unique capability for studying the interaction between strain, surface morphology and microstructural evolution in polycrystalline metal films. The stress monitor will be used to

study the CVD growth of III-nitrides where the ambient gas pressure makes it difficult to use other surface characterization tools.

Interactions with DOE Technologies:

Understanding and controlling the growth of advanced thin film structures supports DP research and development programs, e.g., monitoring stress in thin films is critical for predicting effects of aging. A patent application has been filed for the multi-beam optical stress sensor, and a commercialization agreement for the manufacture and sale of a system using this technique is being negotiated.

Program Quality

Outstanding Scientific Accomplishment in Solid State Physics Award, DOE-BES, Office of Energy Research Young Scientist Award (Brian Swartzentruber); 11 publications, 20 presentations (10 invited), 1 patent application, 2 invited review articles.

Publications

1. Ge SEGREGATION PROFILES DETERMINED BY REAL-TIME SURFACE STRESS MEASUREMENTS DURING SiGe MOLECULAR BEAM EPITAXY, J.A. Floro and E. Chason, Appl. Phys. Lett., in press.
2. KINETICS OF SI MONOMER TRAPPING AT STEPS AND ISLANDS ON SI(001), B.S. Swartzentruber, Phys. Rev. B, in press.
3. MONTE CARLO SIMULATIONS OF ION-ENHANCED ISLAND COARSENING, E. Chason and B.K. Kellerman, Nucl. Instr. and Meth. B, in press.
4. EVOLUTION OF SURFACE ROUGHNESS DURING CVD GROWTH, E. Chason, T.M. Mayer, D.P. Adams, H. Huang, T.Diaz De La Rubia, G. Gilmer, B. K. Kellerman , Mater. Res. Symp. Proc. 1997, in press.
5. ION BEAMS IN SILICON PROCESSING AND CHARACTERIZATION, E. Chason, , S.T. Picraux, J.M. Poate, J.O. Borland, M.I. Current, T. Diaz De La Rubia, D.J. Eaglesham, O.W. Holland, M.E. Law, C.W. Magee, J.W. Mayer, J. Melngailis And A.F. Tasch, J. Appl. Phys. Rev. (Invited Review), in press.
6. THIN FILM AND SURFACE CHARACTERIZATION USING SPECULAR X-RAY REFLECTIVITY, E. Chason And T.M. Mayer, Crc Critical Reviews In Materials And Solid State Science (Invited Review), in press.
7. MEASUREMENTS OF STRESS EVOLUTION DURING THIN FILM GROWTH, E. Chason And J.A. Floro, Mater. Res. Symp. Proc., 1996, in press.
8. DECAY OF ISOLATED FEATURES DRIVEN BY THE GIBBS-THOMSON EFFECT IN ANALYTICAL MODEL AND SIMULATION, J.G. Mclean, B. Krishnamachari, D.R. Peale, E. Chason, J..P. Sethna And B.H. Cooper, Phys. Rev. B, in press.
9. ENERGETIC IONS IN SEMICONDUCTOR PROCESSING: SUMMARY OF A DOE PANEL STUDY, S.T. Picraux, E. Chason, J.M. Poate, J.O. Borland, M.I. Current, T. Diaz De La Rubia, D.J. Eaglesham, O.W. Holland, M.E. Law, C.W. Magee, J.W. Mayer, J. Melngailis and A.F. Tasch, Mater. Res. Symp. Proc. 396, 859 (1996).
10. RECIPROCAL SPACE ANALYSIS OF THE INITIAL STAGES OF STRAIN RELAXATION IN SIGE EPILAYERS, S.R. Lee and J.A. Floro, Mat. Res. Soc. Symp. Proc. 399, 455 (1996).

Work Performed Jointly with other programs

11. IN SITU X-RAY REFLECTIVITY INVESTIGATION OF GROWTH AND SURFACE MORPHOLOGY DURING FE CHEMICAL VAPOR DEPOSITION ON SI(001), B.K. Kellerman, E. Chason, T.M. Mayer, D.P. Adams and J.M. White, Surf. Sci., in press.

Patent Applications

1. MEASUREMENT OF THE CURVATURE OF A SURFACE USING PARALLEL LIGHT BEAMS, E. Chason, J.A. Floro, C.H. Seager and M.B. Sinclair, S-85,031/SD-5750, filing date Nov. 25, 1996.

Artificially-Structured Semiconductor Materials Science
KC 02 01 05

Principal Investigators: P. L. Gourley, M. H. Crawford, E. D. Jones M. B. Sinclair, and J. R. Wendt

Goals: Investigate fundamental opto-electronic properties of artificially structured semiconductor materials, including epitaxial layers (molecular beam or vapor phase epitaxy) and surface-structured semiconductors produced by lithography. The former include quantum wells, superlattices, distributed Bragg reflectors, and one-dimensional photonic lattices. The latter include 2-dimensional photonic lattices and 3-D microcavities. Identify, synthesize, and study new artificial materials and structures for efficient light generation with emphasis on scientific and technological impact.

Recent Highlights

- Images and Spectra of Inhibited Light Propagation in a 2-dimensional Photonic Lattice. Using infrared light scattering, transmittance and reflectance microscopy with a tunable, ultrafast laser source, we have directly observed the inhibition of photon propagation in a 2-dimensional photonic lattice fabricated as a hexagonal array of AlGaAs posts. The lattice was formed by reactive ion etching of ~400 nm diameter posts defined by electron beam lithography. The lattice design parameters (post diameter and spacing) correspond to a photonic bandgap near 1.5 um as calculated by Meade et al. The experimental data reveal a distinct bandgap between 1.45 and 1.50 μm with a width of about 4% which is slightly less than theoretical predictions.
- Growth and Study of Visible Light-Emitting InAlGaP Alloys. A number of ~ 1 micron thick $(Al_yGa_{1-y})_{1-x}In_xP$ bulk alloy films were grown by metal-organic vapor phase epitaxy (MOVPE), lattice-matched to misoriented GaAs substrates to reduce atomic ordering. The aluminum composition varied from y-0.1 to 0.5 corresponding to bandgap wavelengths in the yellow, orange, and red. Additional structures with a higher bandgap cladding y-0.7 were also grown to minimize surface recombination of carriers. Luminescence studies of these structures reveal carrier lifetimes of a few hundred picoseconds and that surface recombination is not a dominant recombination mechanism.
- Bandstructure Determinations of 1.6 μm Wavelength Semiconductor Alloys. We have performed the first magnetic-field-dependent infrared photoluminescence studies of heavily doped quantum well structures such as InGaAs/InAlAS latticed matched to InP. Using the Sandia-perfected magnetoluminescence measurement technique, we have measured the conduction-band mass in a InGaAs/InAlAs quantum well with $N_{2D}=2x10^{12}$ cm^{-2} to be 0.068 which is about 50% larger than the undoped bandedge mass. This result collaborates recent cyclotron resonance determinations which gave conduction-band masses of 0.060.
- Ultrafast optical gating technique for studying carrier relaxation. We have designed, constructed, and tested a transient Kerr-effect gate for probing carrier dynamics in semiconductors. The gate relies on transient birefringence, induced in a $SrTiO_3$ plate by a femtosecond laser pulse. The plate is placed between two crossed polarizers and can be "opened" for durations as short as 100 fs. By varying the delay between the laser pumping time of a semiconductor and the opening of the gate to accept its emission, carrier dynamics can be studied.
- Light Emission in Microfabricated Semiconductor/Glass Microcavities. We have studied spontaneous emission from microcavities fabricated for flowing intracavity fluids. Semiconductors surface-emitting structures were coated with ion-beam deposited SiO_2 layers varying in thickness from 50 to 500 nm. These layered structures were covered with a highly reflecting dielectric mirror and optically pumped to observe spontaneous emission spectra. The integrated spectral intensity as a function of layer thickness exhibited a peak near 100 nm, representing a 3-fold enhancement of the intensity. These data demonstrate how insulating layers can be used to tailor the emission from a microcavity.

Future Directions

Near infrared and visible bandgap alloys and quantum well heterostructures will be developed by metal-organic vapor phase epitaxy and molecular beam epitaxy. We will develop new spectroscopic and microscopic methods for assessing optical transitions and energy states, carrier mobility, and structural quality of epitaxial layers. New methods for assessing optical transitions and energy states, carrier mobility, and structural quality of epitaxial layers. New methods for fabricating semiconductor microstructures and nanostructures, including semiconductor/glass combinations will be investigated.

Program Quality

12 Invited talks, 3 invited review articles to, *Optics and Photonics News, Nature/Medicine,* and *OptoElectronic Reports*, 1 patent application, 15 publications, Chairman Microfabrication conference for Photonics West '97, Plenary lecture International Quantum Electronics Conference, International Collaboration through NATO Advanced Study Institute.

Publications

1. SEMICONDUCTOR MICROLASERS: A NEW APPRAOCH TO CELL-STRUCTURE ANALYSIS, P. L. Gourley, Nature Medicine, **2** 942 (1996), invited.
2. INTRACAVITY SPECTROSCOPY IN VERTICAL CAVITY SURFACE-EMITTING LASERS FOR MICRO-OPTICAL MECHANICAL SYSTEMS, K.E. Meissner, P.L. Gourley, T.M> Brennan, B. E. Hammons, and A.E. McDonald, Applied Physics Letters, 69 1517 (1996).
3. IMAGES AND SPECTRA OF INHIBITED LIGHT PROPAGATION IN A 2-DIMENSIONAL PHOTONIC LATTICE AT 1.5 MICRONS, P. L. Gourley, J.R. Wendt, G. A. Vawter, A. E. McDonald, and A.E. Bieber, Proc. Conf. on Lasers and Electro-optics, Anaheim, CA 1996.
4. MANY-BODY EFFECTS IN A SEMICONDUCTOR MICROCAVITY LASER: EXPERIMENT AND THEORY, M. Hagerott Crawford, K.D. Choquette, W.W. Chow and R. P. Schneider, Jr. In Quantum Electronics and Laser Science Conference, Vol. 10, 1996 OSA Technical Digest Series, P. 160.
5. COMPOSITIONAL DEPENDENCE OF THE LUMINESCENCE OF In0.49 (AlyGal-y) 0.51P ALLOYS NEAR THE DIRECT-INDIRECT BAND-GAP CROSSOVER, J.S. Nelson, E.D. Jones, S. M. Meyers, D. M. Follstaedt, H.P. Hjalmarson, J.E. Schirber, R.P. Schneider, J. E. Foquet, V. M. Robbins and K.W. Carey, Phys. Rev. **B53**, 15893 (1996)
6. LOW THRESHOLD AND HIGH TEMPERATURE PERFORMANCE OF SELECTIVELY OXIDIZED VISIBLE VCSELs, M. Hagerott Crawford, K.D. Choquette, R. J. Hickman and K.M. Geib, submitted to the Conference on Lasers and Electro-Optics (CLEO '97), Nov. 1996.
7. A BIOLOGICAL MICROCAVITY LASER, P.L. Gourley and M.F. Gourley, *proc. 20th Int'l Quantum Electronics Conf.*, Sydney, Australia, July 14-19, 1996, invited paper WD7.
8. VERTICAL-CAVITY SURFACE-EMITTING LASERS FOR CYTOMETRY, P.L. Gourley, M>F. Gourley, T. Bocklage, and M. Luke, proc. Conf. on Lasers and Elector-Optics, July 2-7, Anaheim, CA, paper CtuH3, p. 103.
9. INTEGRATION OF MICRO-ELECTRICAL-MECHANICAL SYSTEMS AND MEDICINE,P.L. Gourley and M.F. Gourley, Optical Engineering Reports, **157** 1 (1997), January, invited.
10. TRANSIENT PHOTO-INDUCED ABSORPTION IN AlGaAsP FRACTAL QUANTUM WELL HETEROSTRUCTURES, M.B. Sinclair, P.L. Gourley, M. H. Crawford, K.E. Meissner, and R.P. Schneider, Jr., Applied Physics Letters.

Field-Structured Anisotropic Composites
KC 02 01 05

Principal Investigators: J.E. Martin, R.A. Anderson, and C.P. Tigges

Goals: We will develop the modeling, synthesis, and processing capability to create novel anisotropic polymer/ceramic and polymer/metal composite materials by applying external electric or magnetic fields to systems consisting of a polymerizable continuous phase into which particles having an electric permittivity or magnetic permeability mismatch are suspended.

Recent Highlights:

- Modeling of one-dimensional nanocomposites. We have developed a Langevin dynamics simulation of hard spheres with induced dipolar interactions and Stokes friction against the solvent. We have simulated the concentration dependence (volume fractions from 5% to 60%) of structural evolution, with data out to 1000 ms for 1000 spheres and to 150 ms for 10000 spheres. A principal conclusion of these simulations is that structural coarsening is driven by defects. Extant theories attribute coarsening solely to the mode coupling of thermal fluctuations.
- Computation of properties of one-dimensional nanocomposites. We have computed, as functions of time, 2-D pair correlation functions, dipolar interaction energies, microcrystalline domain growth, and the anisotropy of the conductivity, capacitance, and optical transmission. These studies demonstrate the potential for controlling the properties of field-structured composites; the capacitance, electric and thermal conductivity, and optical transmission increase greatly along the field axis.
- Synthesize 1-D polymer/ceramic nanocomposites. We have made electric field-structured samples with particulates having a range of dielectric constants, viz. titania, strontium titanate, and barium titanate (a ferroelectric). We have systematically varied the particulate loading from 10 wt % to 75 wt %. We have prepared a number of samples in epoxy using magnetic iron oxide particles of different sizes. We varied the magnetic field quench time to control the coarsening, and added nonmagnetic, dielectric particles to increase the fluid friction and reduce coarsening.
- Determine structure from the complex permittivity. We made complex permittivity measurements of all the dielectric samples, both along the applied field (z-axis) and orthogonal to it (x-y plane). These measurements show that the dielectric constant along the z axis is about 2-3 times as great as in the x-y plane, and that in the x-y plane the dielectric constant was about the same as in the control sample. These results are in agreement with the dielectric anisotropy we obtain from simulations. Simulations of structure formation in a rotating field applied in the x-y plane invert the anisotropy: the dielectric constant being 2-3 times higher in the x-y plane than along the z-axis. Magnetic susceptibility measurements on the iron oxide samples showed pronounced anisotropy as well, the largest effect being a significant increase in the remnant magnetization along the z-axis.
- Time-resolved, two-dimensional light scattering measurements. Light scattering data on a refractive index matched silica ER fluid show a well defined peak in the structure factor that enables us to follow coarsening in detail. At high particle concentrations the scattering anisotropy rapidly decreases, in a manner similar to scattering functions we have computed from our simulated structures.
- Modeling of two-dimensional nanocomposites. This code is technically similar to the uniaxial field case, but the field rotates in the x-y plane on a time scale fast compared to the time it takes a particle to diffuse its own radius. Whereas the uniaxial field (applied along the z-axis) generates column-like structures, the rotating field generates sheets. These sheets have the opposite dielectric anisotropy as the columns, having a higher dielectric constant in the plane.

Future Directions:

We will implement temperature into the computer modeling algorithms for one and two-dimensional nanocomposites. We will synthesize electric field quenched 2-D polymer/ceramic composites and magnetic

field quenched 2-D polymer/metal or metal oxide nanocomposites. We will characterize the anisotropy of the composites by conductivity, optical attenuation, and permittivity.

Interactions with DOE Technologies:

This research was motivated by the potential of materials with tailored anisotropies for DP components, and it interacts with one of the component development programs. This research was initiated as an LDRD program. BES funding to continue the work was started in mid 1996. The above accomplishments are joint with the LDRD program.

Program Quality:

2 publications, 4 presentations, including 2 invited talks.

Publications

This is a new activity initiated in mid 1996. The following two manuscripts are joint with an LDRD-funded activity.

1. SIMULATION OF ATHERMAL COARSENING IN INDUCED DIPOLAR FLUIDS: UNIAXIAL FIELDS, Martin J E, Anderson R A and Tigges C P, preprint.
2. SIMULATION OF ATHERMAL COARSENING IN INDUCED DIPOLAR FLUIDS: ROTATING FIELDS, Martin J E, Anderson R A and Tigges C P, preprint.

Materials Science and Physics of Tl-Ba-Ca-Cu-O Superconductors
KC 02 02 02

Principal Investigators: B. Morosin, P. P. Newcomer, J. E. Schirber, M. P. Siegal, and E. L. Venturini

Goals: We are defining controlled processes for the growth of high-quality, single phase Tl-Ba-Ca-Cu-O thin film superconductors based on knowledge developed at Sandia of both thermodynamics and kinetics. Focused experiments are providing a fundamental understanding of the intrinsic properties of these films and are optimizing their extrinsic properties, including the structural defects required for enhanced vortex pinning and critical current density.

Research Highlights:

- Controlled growth of Tl-Ba-Ca-Cu-O thin films: High-quality single-phase Tl-Ba-Ca-Cu-O thin films of each of the four major superconducting phases are produced using a new, simplified version of the Sandia crucible process. Both the thermodynamics and kinetics of growth must be taken into consideration.
- New manufacturable Tl-Ba-Ca-Cu-O thin film process (Patent Caution): A scalable two-zone furnace process has been developed that allows higher throughput and minimizes handling of hazardous Tl-oxides compared to existing processes.
- High-energy heavy-ion irradiation: HRTEM images reveal differences in microstructural damage for $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) thin films as a function of the ion energy loss rate dE/dx. Linear amorphous tracks are generated by 88 MeV Au ions (dE/dx ~ 20 keV/nm) while irregular, extended defects are produced by 60 MeV Cu ions (dE/dx ~ 12 keV/nm). However, there is significant collateral damage and related strain due to secondary ions from collision events within the primary ion track. Our results suggest that Cu ions are preferable for extrinsic defects to enhance vortex pinning in highly anisotropic materials such as Tl-2212.
- Microstructure of furnace-annealed Tl-1212 films: Simple post-growth furnace anneals in various gas ambients produce significantly enhanced T_c's, critical current densities and vortex pinning in $TlBa_2CaCu_2O_8$ (Tl-1212) thin films. HRTEM images reveal clustered defects in the form of pinched stacking faults attributed to localized loss of TlO_x during annealing. These nanoscale defects may be the source of the improved superconducting properties.
- Rb-doped Tl-Ba-Ca-Cu-O single crystals: Single crystals of the four principal Tl-Ba-Ca-Cu-O superconducting structures have been grown from fluxes containing up to 30 mole % Rb_2O. Structural and energy-dispersive x-ray analyses indicate that up to 10% of the Tl is replaced by Rb; atomic parameters typically show small differences resulting from the local growth environment and the crystals are usually thicker than Rb-free specimens. Magnetic measurements show that Rb doping has a negligible effect, i.e., T_c values and transition widths are not altered by Rb substitution at Tl sites.
- Annealing of Tl-1212 crystals: Annealing studies under flowing argon and/or oxygen on Tl-Ba-Ca-Cu-O single crystals with the Tl-1212 structure demonstrate small structural changes consistent with our previously reported Tl^{+1}/Tl^{+3} equilibrium charge-reservoir model for Tl-containing superconductors.
- New Materials: We have demonstrated that for Na_2CsC_{60} certain pressure/temperature protocols result in the reversible formation of a superconducting polymeric orthorhombic structural phase, challenging earlier theoretical models for such alkali-intercalated C_{60} compounds. Collaborative neutron diffraction experiments have determined the phase diagram.

Future Directions:

We will continue our primary emphasis on the thermodynamics and kinetics of Tl-based thin film growth and on the physics of superconductivity in these films and related superconducting materials. Combined structural and magnetization studies will enhance our understanding of both the intrinsic and extrinsic properties, leading to optimized films for device applications through control of the microstructure. We are pursuing several collaborations to access novel experimental techniques and expertise that will enhance our knowledge of these promising materials.

Technical Interactions:

Defense Programs: superconducting films for microwave components (filters and delay lines for radar and communications applications). Energy Efficiency and Renewable Energy: growth techniques for oriented Tl-based films on inexpensive, flexible substrates. Active research collaborations with universities: optical properties (Maryland), HRTEM (New Mexico) and vortex dynamics (New Mexico Highlands); industry: DuPont Superconductivity, Conductus and Varian; government labs: neutron scattering (ANL, LANL), photoemission (JPL), film growth (NREL).

Tech Transfer:

Research supported by this BES program prompted and leveraged a Technology Transfer Initiative CRADA with DuPont to develop a new manufacturing process for Tl-based high-T_c superconducting thin films.

Program Quality and Impact:

2 patent disclosure, 2 invited presentations, 12 publications.

Publications

1. STABILITY OF THE TL-1223 PHASES, T.L. Aselage, E.L. Venturini, J.A. Voigt And D.J. Miller, J. Mater. Res. 11 1635 (1996).
2. EFFECT OF PRESSURE ON THE SUPERCONDUCTING PRIMITIVE CUBIC AND 'POLYMERIC' PHASES OF NA2CSC60, J.E. Schirber, L.V. Hansen, B. Morosin, J.E. Fischer, J.D. Jorgensen And G.H. Kwei, Physica C 260 173 (1996).
3. TEMPERATURE-DEPENDENT MICROSTRUCTURAL MODIFICATION IN ION-IRRADIATED TL-TYPE HIGH-TEMPERATURE SUPERCONDUCTORS, P.P. Newcomer, L.-M. Wang, J.C. Barbour, R.C. Ewing, M.L. Miller And B. Morosin, Physica C 267 243 (1996).
4. IMPORTANCE OF THERMODYNAMICS AND KINETICS IN THE GROWTH OF THIN FILM Tl-Ba-Ca-Cu-O SUPERCONDUCTORS, M.P. Siegal, D.L. Overmyer, E.L. Venturini, P.P. Newcomer, R.G. Dunn, F. Dominguez, R.R. Padilla And S.S. Sokolowski, IEEE Trans. On Supercond., To Appear (Invited).
5. ENHANCED VORTEX PINNING IN ANNEALED Tl-Ba_2-Ca-Cu_2-O_X THIN FILMS, E.L. Venturini, P.P. Newcomer, M.P. Siegal And D.L. Overmyer, IEEE Trans. On Supercond., To Appear.
6. MICROSTRUCTURE IN TL-1212 THIN FILMS AFTER REDUCING ANNEALS WHICH ENHANCED CRITICAL CURRENT DENSITIES, P.P. Newcomer, M.P. Siegal, E.L. Venturini And D.L. Overmyer, IEEE Trans. On Supercond., To Appear.
7. STRONGLY ENHANCED VORTEX PINNING IN HIGH-ENERGY, HEAVY-ION-IRRADIATED, SUPERCONDUCTING Tl-Ba-Ca-Cu-O FILMS, E.L. Venturini, P.P. Newcomer, H. Schöne, B.L. Doyle And K.E. Myers, Nucl. Instrum. Meth. Phys. Res. B, To Appear.
8. ON THE PRESSURE INDUCED PHASE OF Na_2CSC_{60}, B. Morosin, J.E. Schirber, J.D. Jorgensen, G.H. Kwei, T. Yildirim And J.E. Fischer, To Appear In Science And Technology Of Fullerene Materials Iii (Invited).
9. ON TL-2212 SUPERCONDUCTOR SINGLE CRYSTALS: STRUCTURE AND MAGNETISM CHANGES ON ANNEALING, B. Morosin, E.L. Venturini, R.G. Dunn And P.P. Newcomer, Submitted To Physica C.

10. STRUCTURAL AND COMPOSITIONAL CHARACTERIZATION OF RUBIDIUM-CONTAINING CRYSTALS OF THE Tl-Ba-Ca-Cu-O SUPERCONDUCTORS, B. Morosin, E.L. Venturini, R.G. Dunn, P.P. Newcomer, N. Missert And R.R. Padilla, In Preparation.

Work Performed Jointly with Other Programs

11. STRUCTURE OF $CE_2PT_6GA_{15}$: INTERPLANAR DISORDER FROM CE_2GA_3 LAYERS, G.H. Kwei, A.C. Lawson, A.C. Larson, B. Morosin, E.M. Larson and P.C. Canfield, Acta Crystall. B 52 580 (1996).

12. ELECTRONIC STRUCTURE OF $TLBA_2CACU_2O_{7-*}$, R.P. Vasquez, D.L. Novikov, A.J. Freeman and M.P. Siegal, submitted to Phys. Rev. B.

Tailored Surfaces And Interfaces For Materials Applications
KC 02 02 02

Principal Investigators: G. L. Kellogg, P. J. Feibelman, T. M. Mayer, and B. S. Swartzentruber

Goal: To understand the atomic-level processes that control the growth of crystalline solids and surface films and learn how to tailor fundamental growth properties for advanced materials applications.

Recent Highlights

- The Effect of Hydrogen on Surface Atom Mobility - Field ion microscope experiments show that the presence of hydrogen increases the rate of hopping displacements for individual Rh atoms migrating on Rh(100), but decreases the rate of exchange displacements for Pt on Pt(100). In the latter case, hydrogen actually changes the preferred diffusion mode form exchange to hopping, suggesting that hydrogen may be used to suppress interfacial intermixing.
- Oxygen Binding at Atomic Steps on Platinum Surfaces - We used QUEST, our massively-parallel, first-principles total energy code, to discover and interpret oxygen binding-site preferences on stepped-Pt(111) surfaces. The calculations account remarkably well for the very different STM images of oxygen that correspond to the two types of close-packed steps on this surface, and they explain the source of the different bonding configurations. These studies provide new insight into how oxygen may be used as a surfactant to facilitate layer-by-layer growth.
- Site-Specific Energetics of Silicon Surface Kinetic Processes - Using the high spatial and time resolution of the atom-tracking STM, we measured the rotation rate of adsorbed Si dimers at single lattice sites and their binding free energy near steps and islands. The site-to-site variation of the binding and configurational energy of the dimers is less than a tenth of the activation barrier for dimer diffusion. Such high-resolution measurements are crucial for developing and validating first-principles calculations of growth processes in semiconductor materials systems.
- Interfacial Hydrogen Effects on Aluminum Nucleation and Growth - We have observed a change in growth mode for Al on clean vs. H-terminated Si(001). STM images show that on clean Si, an ordered 2x2 overlayer of Al dimer chains completely wets the Si surface, followed by three-dimensional nucleation of Al islands. On the H-terminated surface, three-dimensional growth proceeds immediately. These results help us understand how to control of structure and morphology of Al films in processing environments in which H is present (CVD, sputtering, etc.).
- Hydrogen-Induced Faceting in Aluminum Epitaxy - Large scale first-principles calculations explain why Al epitaxy leads to rough films in the presence of hydrogen, a common co-adsorbate during growth. With enough hydrogen adsorbed, any flat Al surface is unstable and reconstructs into microfacets with a high concentration of steps and vacancies. The new morphology reduces the surface mobility and thus alters the kinetics of growth.
- New Capability in Low Energy Electron Microscopy (LEEM) - Our newly acquired LEEM is now fully operational. The spatial resolution is <10 nm -- better than all other existing LEEMs.

Future Directions

This program will continue to focus on understanding the microscopic mechanisms that control the growth and stability of crystalline solids and thin surface films. A major emphasis will be placed on learning how to manipulate and direct thin-film growth through the use of chemical adsorbates or "surfactants." Atomic-scale experimental and theoretical investigations will provide detailed information on the mechanisms and energetics of elementary steps in the growth process and the changes that occur with the addition of adsorbed atoms and molecules. Our recently developed "atom-tracker" STM will be used to investigate the strength and spatial extent of surface interactions using an individual atom as a probe. Our newly acquired low energy electron microscope (LEEM) will be used to test the predictions of growth models based on our atomic-level understanding.

Interactions with DOE Technologies:

This BES-supported research is providing both fundamental understanding and quantitative input required to develop science-based models of materials growth and stability. Interactions with DP-funded R&D programs addressing the long-term stability of materials will lead to more reliable predictions of component reliability and safety.

Program Quality

- Medard W. Welch Award of the American Vacuum Society
- 1996 DOE/BES/MS Outstanding Scientific Accomplishment in Solid State Physics
- DOE Office of Energy Research's Young Scientist Award
- 15 Invited Presentations at National and International Conferences
- 12 publications

Publications

1. HYDROGEN PROMOTION OF SURFACE SELF-DIFFUSION ON Rh(100) AND Rh(311), G. L. Kellogg, Phys. Rev. B (in press).
2. AN ATOMIC VIEW OF CLUSTER DIFFUSION ON METAL SURFACES, G. L. Kellogg, Progress in Surface Science (in press).
3. O BINDING SITES ON STEPPED Pt(111) SURFACES, P. J. Feibelman, S. Esch and T. Michely, Phys. Rev. Lett. 77, 2257(1996).
4. A LOCAL VIEW OF BONDING AND DIFFUSION AT METAL SURFACES, P. J. Feibelman, Proceedings of the NATO Advanced Study Institute: Surface Diffusion - Atomistic and Collective Processes, Rodos, Greece, 1996 (in press).
5. H-ENHANCED MOBILITY AND DEFECT FORMATION AT SURFACES: H ON Be(0001), R. Stumpf, Phys. Rev. B 53, 4253R (1996).
6. RECONSTRUCTION AND FACETING OF H-COVERED Al(111), R. Stumpf, Phys. Rev. Lett. (submitted).
7. EXPERIMENTAL AND THEORETICAL STUDY OF THE ROTATION RATE OF SI AD-DIMERS ON THE Si(001) SURFACE, B. S. Swartzentruber, A. P. Smith, and H. Jónsson, Phys. Rev. Lett. 77, 2518 (1996).
8. Si AD-DIMER INTERACTIONS WITH STEPS AND ISLANDS ON Si(001), B. S. Swartzentruber, Surface Sci. (in press).

Work Performed Jointly with Other Programs

9. TOWARDS AN UNDERSTANDING OF LIQUID METAL EMBRITTLEMENT: ENERGETICS OF Ga ON Al SURFACES, R. Stumpf and P. J. Feibelman, Phys. Rev. B54, 5145(1996).
10. ISLAND STRUCTURE EVOLUTION DURING CHEMICAL VAPOR DEPOSITION, D. P. Adams, T. M. Mayer, E. Chason, B. K. Kellerman, and B. S. Swartzentruber, Surface Sci. (in press).
11. *IN SITU* X-RAY REFLECTIVITY INVESTIGATION OF GROWTH AND SURFACE MORPHOLOGY EVOLUTION DURING Fe CHEMICAL VAPOR DEPOSITION ON Si(001), B. K. Kellerman, E. Chason, D. P. Adams, T. M. Mayer, J. M. White, Surface Sci. (in press).
12. EVOLUTION OF SURFACE ROUGHNESS DURING CVD GROWTH, E. Chason, T. M. Mayer, D. P. Adams, H. Huang, T. Diaz de la Rubia, G. Gilmer, B. K. Kellerman, Mater. Res. Soc. Proc. (in press).

Spontaneous Composition Modulation Studies in Compound Semiconductors*
KC 02 02 02

Principal Investigators: E. D. Jones, J. L. Reno, A. M. Mascarenhas, and A. Zunger

Goals: Investigate the fundamental properties and origins of spontaneous composition modulation in compound semiconductor epilayers and superlattices. Study and quantify the root causes of composition modulation. Identify, synthesize, and study the electrical, transport, and optical properties of new material systems for efficient photovoltaic and polarized-laser applications.

Recent Highlights

- Lateral Spontaneous Composition Modulation in InAs/AlAs Short Period Superlattices. Using molecular beam epitaxy growth techniques, we have discovered lateral composition modulation in monolayer-sized superlattices of InAs/AlAs on InP. The period of the lateral composition wave is of the order of 200Å. A variety of experimental techniques, including transmission electron microscopy, x-ray reciprocal space analysis and polarized-photoluminescence measurements were used to verify, and quantify the nature and properties of the composition modulation.
- Advanced Characterization Techniques. In order to detect, verify, and quantify the presence of composition modulation in a rapid manner, we have developed two new experimental techniques, x-ray reciprocal space analysis and angular-dependent magnetoexciton spectroscopy. The x-ray reciprocal space analysis technique provides detailed information about the amount of residual strain and the size and direction of the composition modulation wave. Recently, we have applied an old technique, magnetoexciton spectroscopy, to detect, and study lateral composition modulation in InAs/GaAs short period superlattices lattice matched to GaAs with the result that an unambiguous signature for composition modulation was discovered.

Future Directions

There are three parts for future directions: (1) Determine the methodology for controlling the wavelength and amplitude of the composition modulation region, (2) Extending current studies (growth and characterization) to larger bandgap alloys systems such as InAsN, and (3) Study the effects of incorporating the varying the stress/strain and composition modulation parameters to obtain type-II (spatially indirect) band alignments for advanced photovoltaic material systems.

Program Quality

One Conference Proceedings Book, an Invited Review article for the Materials Research Bulletin, two Invited Conference talks, and seven conference presentations.

Publications

Microstructure of compositionally modulated InAlAs, R. D. Twesten, J. Mirecki Millunchick, S. P. Ahrenkiel, Y. Zhang, D. M. Follstaedt, A. Mascarenhas, and E. D. Jones, Proceedings of the Materials Research Society, Boston, MA, Dec. 2-6, 1996.

1. OPTOELECTRONIC MATERIALS - ORDERING, COMPOSITION MODULATION, AND SELF-ASSEMBLED STRUCTURES, Edited by E. D. Jones, A. Mascarenhas, and P. Petroff, Volume 417, Materials Research Society Symposium Proceedings, Pittsburgh 1996.

* Joint Project with NREL.

2. COMPOSITION MODULATION IN AlAs/InAs SHORT PERIOD SUPERLATTICES GROWN ON InP(001), J. Mirecki Millunchick, R. D. Twesten, D. M. Follstaedt, S. R. Lee, E. D. Jones, Y. Zhang, S. P. Ahrenkiel, and A. Mascarenhas, Appl. Phys. Lett. (1997).
3. STRUCTURAL AND OPTICAL CHARACTERIZATION OF COMPOSITION MODULATION IN InAlAs AND InGaAs LAYERS ON InP(001), J. Mirecki Millunchick, R. D. Twesten, D. M. Follstaedt, S. R. Lee, E. D. Jones, Y. Zhang, H. M. Cheong, S. P. Ahrenkiel, and A. Mascarenhas, Appl. Phys. Lett. (1997).
4. DETECTION OF LATERAL COMPOSITION MODULATION N A $(InAs)_n/(GaAs)_n$ SHORT PERIOD SUPERLATTICE ON InP BY MAGNETOEXCITON SPECTROSCOPY, E. D. Jones, J. Mirecki-Millunchick, D. Follstaedt, M. Hafich, S. Lee, J. Reno, R. Twesten, Y. Zhang, and A. Mascarenhas, SPIE Photonics West '97: Physics and Simulation of Optoelectronic Devices V, 8-14 February 1997, San Jose, CA, Physics and Simulation of Optoelectronic Devices V SPIE Vol.
5. SPONTANEOUS LATERAL COMPOSITION MODULATION IN III-V SEMICONDUCTOR ALLOYS, J. Mirecki Millunchick, R. D. Twesten, S. R. Lee, D. M. Follstaedt, E. D. Jones, S. P. Ahrenkiel, Y. Zhang, H. M. Cheong, and A. Mascarenhas, MRS Bulletin (1997).
6. SPONTANEOUS COMPOSITION MODULATION IN AlAs/InAs SHORT PERIOD SUPERLATTICES, J. Mirecki Millunchick, R. D. Twesten, S. R. Lee, D. M. Follstaedt, E. D. Jones, S. P. Ahrenkiel, Y. Zhang, H. M. Cheong, and A. Mascarenhas, J. Electronic Materials (1997).

Transport In Unconventional Solids
KC 02 02 05

Principal Investigators: T. L. Aselage, D. Emin, S. S. McCready, H. Brom, D. Evans and D. R. Tallant

Goals: We seek to understand and exploit novel aspects of electronic transport in solids whose bonding and/or structures promote unusually strong interactions between charge carriers and their surrounding atoms. As a result of these interactions, electronic transport in unconventional solids is distinct from solids in which charge carriers move quasi-freely.

Highlights

- The temperature dependences of boron carbides' Seebeck coefficients we measure between 15K and 900K are distinctive. The Seebeck coefficients rise rapidly with temperature at low temperature, reach a maximum near 200K, and then gradually fall to a nearly temperature-independent plateau. We have shown that this unusual dependence mirrors the sum of two novel effects associated with carriers softening the sites on which they reside. The change in vibrational entropy that accompanies softening yields a Seebeck coefficient that rises to a plateau. An additional contribution is associated with the portion of the hopping activation energy transferred with a carrier as it hops from its softened site. This contribution to the Seebeck coefficient peaks at the temperature below which the hopping mobility becomes non-Arrhenius, about 200K in boron carbides.
- Cavities within clathrate networks incorporate interstitial cations that bind electrons to the surrounding cage atoms. These states are similar to those of boron icosahedra. There is limited evidence (ca. 1970) of unexpectedly large Seebeck coefficients in some clathrates. Facilities were designed and prepared for clathrate synthesis. Measuring electronic transport of our samples permits assessing whether clathrates' Seebecks are enhanced by the carrier-induced softening found in boron carbides.
- Calibrated NMR intensities obtained from ^{13}C-enriched boron carbides were compared to the densities of carbon atoms. We measure that an increasing portion of icosahedral carbons' NMR signal is lost as densities of localized holes increase. Thus we have shown that densities of localized charge carriers can be directly measured with NMR.
- The Seebeck coefficient depends on the number of holes per active site, $B_{11}C$ icosahedra in boron carbides, rather than the number of holes per unit volume, measured by the conductivity. The dependence of boron carbides' high-temperature Seebeck coefficient on carbon concentration is therefore sensitive to carbons' locations. The Seebeck coefficient minimum that we measure at 13 atomic percent carbon implies that carbon atoms remain within icosahedra even below this composition.
- The high-temperature Seebeck coefficient measured in p-type $LaMnO_3$ is much too small to be due to holes moving between the presumed active sites, Mn ions. However, the small Seebeck coefficient is consistent with holes that move only between sites near dopants. We have shown that hopping between dopant-related sites can also give the experimentally observed n-type Hall effect sign anomaly. In contrast, hopping among all Mn sites should give a normally signed, p-type Hall effect.
- Drift velocities of carriers hopping in disordered solids rise dramatically with electric field strength in high fields. This rise is not understood. We developed a general method to calculate the current driven by an electric field in the presence of disorder. Evaluation for several models shows a strong increase of the current with field strength. Since disorder in boron carbides is unusually well characterized, we hope to correlate details of disorder with currents' field- and temperature-dependences.

Future Directions

• Electronic structure studies will be used to determine the fundamental reasons for the large carrier-induced softening of icosahedra. • Clathrate samples will be synthesized and their transport properties measured and analyzed for evidence of carrier-induced softening contributions. • Analytic and computer-based electron structure studies will be used to determine why and when electrons pair as singlets on hollow, cage-like structures (e.g., icosahedra, interstices in networks). • P-type octahedral borides will be synthesized and

their electronic and magnetic properties studied to determine whether carriers on boron octahedra form polarons or bipolarons. • Taken together, separate reports of conductivity and Seebeck effect and of conductivity and Hall effect of $Y_2Ti_2O_7$ pyrochlores are consistent with the carriers forming pairs: mobile large bipolarons. Materials will be prepared and transport measured on common samples. • Transport capabilities will be augmented by building a Hall effect apparatus for 4-300K measurements in 10T fields. • We will study how different models of disorder affect the field and temperature dependences of non-Ohmic hopping-type currents. • Low-temperature/high-field measurements of boron carbides' hopping conduction will be initiated. • Boron carbides' low-temperature non-Arrhenius hopping transport will be analyzed in terms of 1) freezing-out of the pair-breaking mode of small-bipolaron hopping, 2) freezing out of multiphonon hopping, and 3) percolation effects associated with boron carbides' disorder.

Program Quality

- Invited to write articles for Rev. Mod. Phys., Intl. J. Mod. Phys., McGraw-Hill Science Encyclopedia, Mott Festschrift.
- Members of Committees on: Boron, Borides & Related Compounds.; Boron in USA; Hopping & Related Phenomena.
- 12 invited talks (7 meetings and 5 colloquia), 7 publications.
- Industrial Interactions: Dow Chem., Lucent, Textron Spec. Matls, Avalon Spec. Matls, Hi-Z Tech., Constellation Tech.

Publications

1. BREAKDOWN OF THE RESISTOR-NETWORK MODEL FOR STEADY-STATE HOPPING CONDUCTION, David Emin and C. Kuper, Czechoslovak Journal of Physics, 46 Supplement S5, 2431 (1996).
2. HOPPING CONDUCTION IN HIGH ELECTRIC FIELDS: THREE ISSUES, David Emin, SPIE Proceedings Series, Volume 2850 (1996) pp. 159-170.
3. RAMAN SPECTRA OF ISOTOPICALLY ENRICHED $B_{12}As_2$, $B_{12}P_2$, $B_{12}O_2$ AND $B_{12+x}C_{3-x}$: COMPOSITIONS AND RELATIVE STIFFNESS OF ICOSAHEDRA AND CHAINS, T. L. Aselage, D. R. Tallant and David Emin, Physical Review B (submitted).
4. STRUCTURES OF THE BORON-RICH BORON CARBIDES FROM NEUTRON POWDER DIFFRACTION: IMPLICATIONS FOR THE NATURE OF THE INTER-ICOSAHEDRAL CHAINS, G. Kwei and B. Morosin, Journal of Physical Chemistry, 100, 8031 (1996).

Work Performed Jointly with Other Programs

5. HALL EFFECT SIGN ANOMALY AND SMALL-POLARONIC CONDUCTION IN $(La_{1-x}Gd_x)_{0.67}Ca_{0.33}MnO_3$, M. Jaime, H. T. Hardner, M. B. Salamon, M. Rubenstein, P. Doresy and D. Emin, Physical Review Letters (in press).
6. ANOMALOUS HALL EFFECT IN Gd-DOPED $La_{2/3}Ca_{1/3}MnO_3$, M. Jaime, H. T. Hardner, M. B. Salamon, M. Rubenstein, P. Doresy and D. Emin, J. of Magnetism and Magnetic Materials (in press).
7. METAL GETTERING BY BORON SILICIDE PRECIPITATES IN BORON-IMPLANTED SILICON, S. M. Myers, G. A. Petersen, T. J. Headley, J. R. Michael, T. L. Aselage and C. H. Seager, Nuclear Instruments and Methods B. (in press).

CVD Sciences
KC 02 03 03

Principal Investigators: M. E. Coltrin, K. C. Baucom, M. E. Bartram, W. G. Breiland, J. R. Creighton, J. Han, P. Ho, H. K. Moffat, and J. Y. Tsao

Goals: To advance the understanding of the basic physics and chemistry of thin-film synthesis by Chemical Vapor Deposition (CVD), including metalorganic CVD (MOCVD). The program includes the development of new measurement techniques and theoretical tools that can be used both for fundamental scientific studies and for improvements of CVD processes and equipment that can be transferred to industry.

Recent Highlights:

- *In situ* growth rate monitors: A method has been devised to extract the growth rate and chemical composition of a growing semiconductor alloy film from a normal incidence reflectance spectrum. Composition is deduced from the reflectance spectrum by fitting to a model linking the composition of the alloy to its optical constants as a function of wavelength and temperature.
- Temperature hysteresis in a rotating-disk reactor: A natural-convection-induced flow instability in a rotating disk was discovered experimentally and explained using our massively parallel MPSalsa code. Under certain conditions, the azimuthal symmetry in the reactor is broken by a Hopf bifurcation to create a time-dependent flow with period-two 180° reflection symmetry.
- Mechanisms for nitrogen incorporation in GaN MOCVD: We have used surface-sensitive probes to reveal favorable and unfavorable surface interactions between reactants and decomposition products likely to be present during GaN MOCVD. While reactions with gallium alkyls may be important for ammonia uptake and the promotion of contiguous gallium-nitrogen-gallium bonding, sterically-constrained alkyl groups can inhibit the initial nucleation step of gallium-nitrogen bond formation.
- GaN materials synthesis for UV optoelectronics: With the use of a vertical rotating disc CVD reactor with *in-situ* optical reflectometer, we were able to record the evolution of growth morphology. The *in-situ* optical probes provide simple yet instant and crucial information on surface morphological transients. GaN epilayers with defect density comparable to the lowest reported to date (in the mid $10^8 cm^{-2}$) have been obtained in our laboratory.
- In-situ reflectance-difference spectroscopy (RDS) validates MOCVD site-blocking model: Under typical growth conditions around 640°C, the GaAs(100) surface exhibits an RD spectrum that is indicative of a "super" arsenic-rich reconstruction. The magnitude of this peak increases with increasing V/III ratio, and is thus qualitatively consistent with the arsenic site-blocking MOCVD model we developed previously. RDS results also indicate that tertiarybutylarsine is twice as effective as arsine at populating a specific excess arsenic coverage. This result quantitatively agrees with the GaAs MOCVD site-blocking model.
- Model for roughness in thin-film growth: A simple model was developed for morphology evolution in the growth of polycrystalline thin films, from the initial nucleation seeds through coalescence into a columnar grain structure. The model was combined with a model of light scattering from a rough surface, and qualitatively explains the measured evolution of film morphology during GaN growth.
- AlAsSb materials synthesis for environmental sensing: Great advances in composition and morphology control during growth of AlAsSb narrow band-gap semiconductors have been achieved using rotating disk reactor and in-situ optical reflectance monitoring technology. Fatal Al-contamination between AlAsSb/InAs layers has been eliminated, making practical continuous growth of multiply stacked LED and laser devices.
- Thermochemistry of Si-B-H-Cl compounds for understanding in-situ doping in Si CVD: We have used quantum chemistry to obtain thermochemical parameters for more than 90 molecules in the Si-B-H-Cl system. These calculations show that the energy required to eliminate H_2 from silylborane is significantly lower than that required for the analogous reaction in disilane. This suggests that B on the surface eases elimination of H_2 from a silicon surface, and can help explain how small amounts of dopants used in *in-situ* doped CVD can have substantial effects on deposition rates.

Future Directions:

We will pursue the development of new diagnostic tools to probe the details of deposition chemistry relevant to CVD, with an emphasis on tools that monitor the deposition process *in situ*. We will seek to uncover links between process operation parameters and (1) grown-material properties, and (2) performance of the material in its ultimate application. Applications of new diagnostic and computational tools will serve as the basis for developing first-principles models of the complex chemically reacting flows typical of CVD.

Program Quality:

13 publications, 16 presentations, including 7 invited talks at national or international symposia.
This work has led to 8 DP-funded CRADAs and 2 ARPA-funded program with industry.

Publications

1. TEOS SURFACE CHEMISTRY ON SiO_2 AT CVD TEMPERATURES AND PRESSURES, M. E. Bartram, H. K. Moffat, Proceedings of the 13th International. Conference on Chemical Vapor Deposition, The Electrochemical Society, 96-5, 843 (1996).
2. IN SITU PRE-GROWTH CALIBRATION USING REFLECTANCE AS A CONTROL STRATEGY FOR MOCVD FABRICATION OF DEVICE STRUCTURE, W. G. Breiland, H. Q. Hou, H. C. Chui, B. E. Hammons, Proceedings of the 10th American Conference on Crystal Growth, to be published in the Journal of Crystal Growth, 1996.
3. TWO-DIMENSIONAL IMAGING OF LASER INDUCED FLUORESCENCE: OH IN A PLASMA-GENERATED MOLECULAR BEAM SCATTERING FROM A SILICON SURFACE, R. J. Buss, P. Ho, IEEE Transactions in Plasma Science, February, 1996.
4. MATERIALS SYNTHESIS AND PROCESSING, P. Esherick, Introduction to Special Edition of Journal of Materials Research, 11,783 (1996).
5. DEPOSITION CHEMISTRY: DEPOSITION PATHWAYS, NUCLEATION AND GROWTH DIAMOND THIN FILMS HANDBOOK, D. S. Dandy, M. E. Coltrin, J. Asmussen & D. Reinhard, Eds., Marcel Dekker Publishers, to appear.
6. SIMPLIFIED MODELS OF GROWTH, DEFECT FORMATION, AND THERMAL CONDUCTIVITY IN DIAMOND CHEMICAL VAPOR DEPOSITION, M. E. Coltrin, D. S. Dandy, SAND96-0883 (1996).
7. HIGHLY UNIFORM AND REPRODUCIBLE VERTICAL-CAVITY SURFACE-EMITTING LASERS GROWN BY METALORGANIC VAPOR-PHASE EPITAXY WITH *IN-SITU* REFLECTOMETRY, H. Q. Hou, H. C. Chui, K. D. Choquette, B. E. Hammons and W. G. Breiland, IEEE Photonics Technology Letters, 8, 1285, (1996).
8. DEVELOPMENT OF A SCALABLE, FLAT-FLAME TECHNOLOGY FOR THE SYNTHESIS OF DIAMOND FILMS, R. J. Anderson, M. N. Bui-Pham, M. E. Coltrin, D. S. Dandy, C. F. Edwards, D. W. Hahn, R. J. Kee, A. E. Lutz, K. F. McCarty, E. Meeks, and W. S. Winters, SAND96-8215 (1996).
9. SURFACE CHEMKIN-III: A FORTRAN PACKAGE FOR ANALYZING HETEROGENEOUS CHEMICAL KINETICS AT A SOLID-SURFACE - GAS PHASE INTERFACE, M. E. Coltrin R. J. Kee, F. M. Rupley, SAND96-8216 (1996).
10. MP SALSA: A FINITE ELEMENT COMPUTER PROGRAM FOR REACTING FLOW PROBLEMS, PART 1-THEORETICAL DEVELOPMENT, J. N. Shadid, H. K. Moffat, S. A. Hutchinson, G. C. Hennigan, K. D. Devine, and A. G. Salinger, SAND95-2752 (1996).

11. MP SALSA: A FINITE ELEMENT COMPUTER PROGRAM FOR REACTING FLOW PROBLEMS, PART 2-USERS GUIDE, A. G. Salinger, K. D. Devine, G. C. Hennigan, H. K. Moffat, S. A. Hutchinson and J. N. Shadid, SAND96-2331 (1996).

Work Performed Jointly With Other Programs

12. ADVANCED MANUFACTURING TECHNIQUES FOR OPTOELECTRONICS, J. Y. Tsao, R. L. Moon, SAND96-1473 (1996).

13. A REVIEW OF REFLECTION MASS SPECTROMETRY DURING III/V MBE, J. Y. Tsao, Computational Materials Science, 6, 140 (1996).

Synthesis and Processing of Nanoclusters for Energy Applications
KC 02 03 03

Principal Investigators: J. P. Wilcoxon, J. E. Martin, R. Williamson, P. P. Newcomer, G. A. Samara, and T. R. Thurston (BNL)

Goals: Develop synthesis and processing methods for producing chemically pure, highly crystalline mental and semiconductor nanoclusters with controller sizes. Investigate the physical properties of these nanocluster of importance to energy applications such as catalysis.

Recent Highlights:

- Synthesized highly crystalline nanoclusters of MoS_2 and several of its isomorphous Mo and W chalcogenides with excellent control over cluster size down to ~2 nm and investigated their optical properties. Key results include: (1) strong quantum confinement effects with blue shifts as large as 4 eV in some of the absorption features; (2) the quasiparticle (or excitonic) nature of the optical response is preserved down to clusters ≤ 2.5 nm in size which are only two unit cells thick; (3) the demonstration that three-dimensional confinement of the carriers produces energy shifts which are over an order of magnitude larger than those due to one-dimensional (perpendicular to the layer planes) confinement emphasizing the 2-D nature of the structure and bonding; (4) the observation of large increases in the spin-orbit splittings at the top of the valence band and the K and M points of the Brillouin zone with decreasing cluster size, and (5) the observation of photoluminescence due to both direct and surface recombination.
- Discovered that small nanometer size metal clusters exhibit relatively intense visible room temperature photoluminescence (PL), a completely unexpected result. Visible room-temperature PL is commonly observed from semiconductor nanoclusters and is generally shifted to considerably higher energies due to quantum size confinement of the electron-hole pairs. To our knowledge such PL has not been observed from metal nanoclusters before.
- Showed that correct selection of passivating agent could allow us to transfer nanoclusters synthesized in oils to hydrophilic solvents such as ethylene glycol or water. This is an important processing step relevant to the potential application of nanoclusters in catalysis.
- Demonstrated long-term photocorrosion resistance in MoS_2 and WS_2 by exposure to UV fluxes many times that expected from solar sources, and in the presence of molecular O_2. Many samples are now over three years old without detectable changes in size or optical properties.
- Showed that lateral confinement on the planes of MoS_2 and other layered isomorphs is responsible for the large quantum size effects observed in this material. Demonstrated that 3-D confinement effects are much more significant than 1-D confinement thereby emphasizing the influence of dimensionality on quantum confinement.
- Our ability to transfer nanoclusters to various types of solvents by changing the nanocluster surface allowed us to study the effect of solvent polarity on e-transfer efficiency from MoS_2 to organic molecules. Highly polar solvents were found to enhance this efficiency by stabilizing the charge-separated intermediate state.

Future Directions:

Continue investigations of the effect of surface passivating agents and embedding media on photocatalysis and thermal catalysis. Specific studies will emphasize the use of MoS_2 as a photocatalyst when deposited on micron size powders of TiO_2. The optical properties of isomorphous Mo and W dichalcogenides will be investigated in more detail as complements to the work on MoS_2. Thermal catalysis will focus on both base (Ni, Fe, and Mo) and precious (Pt, Pd, and Rh) metal nanosize particles with emphasis on the effect of size and composition on the catalytic activity. Research will continue to identify and understand the origin of our recently observed, tailorable, room temperature, visible light this emission from Si and Ge nanoclusters and to control it in a reproducible manner.

Interactions with DOE Technologies:

New program with ER/EM on use of nanoclusters for photooxidation of organic wastes, continuing our collaboration with D.F. Kelley at Colorado State in this area. New interaction with Palmer's ? (see Dwight) group to study the ordering effects of nanoclusters on substrates using STM. Internal interactions to study films of MoS_2 nanoclusters are micromachine lubricants, and as sprayable metallic inks.

Program Quality:

1996 BES materials science award for Significant Implications for DOE-Related Technologies in Materials Chemistry. 5 publications.

Publications

1. SYNTHESIS AND OPTICAL PROPERTIES OF MoS_2 AND ISOMORPHOUS NANOCLUSTERS IN THE QUANTUM CONFINEMENT REGIME, J.P. Wilcoxon, P.P. Newcomer, and G.A. Samara, J. Appl. Phys., accepted, (1996).
2. INTERFACIAL ELECTRON TRANSFER IN MoS_2 NANOCLUSTERS, F. Parsapour, D.F. Kelley, S. Craft, and J.P. Wilcoxon, J. Am. Chem. Soc., submitted, (1996).
3. OBSERVATION OF PHOTOLUMINESCENCE FROM NANOSIZE GOLD CLUSTERS, J.P. Wilcoxon, J.E. Martin, F. Parsapour, and D.F. Kelley, Phys. Rev. Lett., submitted, (1996).
4. STUDIES OF PHOTOREDOX REACTIONS ON NANOSIZE SEMICONDUCTORS, J.P. Wilcoxon, F. Parsapour, and D.F. Kelley, Proceedings of Symposium Q, MRS, Dec 1996.
5. SYNTHESIS AND OPTICAL PROPERTIES OF MoS_2 AND ISOMORPHOUS NANOCLUSTERS IN THE QUANTUM CONFINEMENT REGIME, J.P. Wilcoxon, P.P. Newcomer, and G.A. Samara, Proceedings of Symposium Q, MRS, Dec 1996.

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