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## A Review of Modern Characterization Methods for Semiconductor Materials

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**A REVIEW OF MODERN CHARACTERIZATION METHODS FOR SEMICONDUCTOR MATERIALS**  
(An Overview of Electron, Ion, X-ray and Optical Probe Characterization Techniques  
Available for Process Diagnostics in the Semiconductor Industry)

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**Abstract**

The manufacture of solid state devices in the microelectronics industry involves crystal growth, slice preparation, diffusion and implantation, oxide and metal deposition, patterning and etching, probe testing and packaging of completed devices. This simplified process flow is adopted in an overview to briefly outline some established as well as newly developed techniques of materials characterization. The complexity of semiconductor processing has imposed greater stringency criteria which have resulted in the revitalization of old methods as well as the development of new techniques capable of extreme sensitivity and spatial resolution.

Examples given for trace impurity and dopant detection include neutron activation analysis, infrared and photoluminescence spectroscopies, atomic resonance ionization, and accelerator based mass spectroscopy. Some methods highlighted for measuring thin film composition and quality are scanning Lang and double crystal x-ray topographies and Rutherford backscattering and Auger spectroscopies. The strengths and frequency of use of these are compared relative to one another and the process steps used in semiconductor manufacture.

**Key words:** Characterization Techniques, Trace Elements, Slice Preparation, Diffusions and Implants, Single Atom Detection, Very Large Scale Integration, Crystal Growth, Characterization Trends, Accelerator Mass Spectroscopy, Resonance Ionization.

**Introduction**

Materials characterization and device development have evolved in a synergistic partnership which has been fundamental to the semiconductor industry. From the partnership has evolved not only a variety of problem solving tools, but also research into aspects of the interaction of probing beams of light, electrons, x-rays and particles with matter. Progressive shrinking of very large scale integrated circuits (VLSI) requires that failure analysis inspections be carried out on tiny defects which are often an order-of-magnitude smaller than the minimum linewidth of the circuit. At the same time, this is accompanied by demand for ultrasensitivity to low level dopant and impurity species.

The need for improved spatial resolution and increased technique sensitivity presents a continual challenge for the characterization specialist, because one requirement is met only at the expense of the other. This is a fundamental constraint in the development of any measurement, and ultimately dictates the function and importance of each machine that is constructed or purchased commercially. The interplay between detectability (signal-to-noise, S/N) and radius of the probing radiation ( $R_0$ ) originates from the familiar expression:

$$\begin{aligned} S/N &\sim \sqrt{\text{number of atoms detected}} \\ &\sim R_0 \end{aligned} \quad (1)$$

in which Poisson statistics are assumed for the analysis physics. This assumption has been fundamental to virtually all of the techniques used in the past but as shown later, modern schemes for detecting single atoms represent a departure from the equation.

Figure 1 shows how methods employing beams of photons, electrons and particles have evolved to optimize the tradeoff between detectability and analytical spot size. Methods that employ tightly focused beams of electrons are applied to circuits where composition and defects are studied with x-y spatial resolutions of 10 to 20,000 Å. The less easily focused beams of ions are useful for trace element detection and determination of thin film composition with quantitative accuracy. Beam of x-rays can be focused only in special experiments and are used where high spatial resolution is not required. They find utility in the measure of material structure and defects. Optical microscopy continues to offer the best low cost approach for rapid nondestructive inspection of surfaces, structure and defects. Spectrometers extend its capability to descriptions of molecular bonding and electronic

Table 1. Capabilities of some commonly used techniques for semiconductor characterization are compared relative to the type of probing radiation. Ia. Optical probes

	Optical Microscopy	Fourier Transform Infrared (FTIR)	Photo Luminescence (PL)	Infrared and Ultra-Violet (IR & UV)	Raman Micro-Probe	Photo-Neutron Activation
Depth Analyzed	> 1-3 $\mu\text{m}$	1-10 mm	1-3 $\mu\text{m}$	1 mm IR 1 $\mu\text{m}$ UV	1 $\mu\text{m}$	0.5 cm
Diameter of Analysis Region	~ 1 cm	2 mm	> 5 $\mu\text{m}$	1 mm	2 $\mu\text{m}$	0.5 cm
Detection Limit (atoms/cm <sup>3</sup> )	visual inspect	1x10 <sup>11</sup>	1x10 <sup>11</sup>	5x10 <sup>18</sup>	5x10 <sup>19</sup>	5x10 <sup>15</sup>
Detection Limit (ppm)	visual inspect	2x10 <sup>-6</sup>	2x10 <sup>-6</sup>	100	1000	0.1
In-depth profiling resolution	none	none	none	none	none	none
Time for Analysis	< 1 hour	2 hours	2 hours	< 1 hour	< 1 hour	2 hours
Comments	In-depth profiling achieved by angle-lap cross section	Performed at 10-15°K temperatures	Performed at 4°K temperatures	Performed at room temperature		Bulk measurement only

Table 1b. Electron beams

	Scanning Electron Microscopy (SEM)	Auger Electron Spectroscopy (AES)	Scanning Auger Microprobe (SAM)	Electron Microprobe (EMP)	Analytical Electron Microscopy (AEM)	High Voltage TEM (HVTEM)
Depth Analyzed	~ 1000 Å	20 Å	20 Å	1 $\mu\text{m}$	< 1000 Å	< 1000 Å
Diameter of Analysis Region	50 Å – 5 mm	100 $\mu\text{m}$	1000 Å	1 $\mu\text{m}$	10 $\mu\text{m}$	10 $\mu\text{m}$
Detection Limit (atoms/cm <sup>3</sup> )	surface image	5x10 <sup>19</sup>	1x10 <sup>21</sup>	5x10 <sup>19</sup>	defect imaging	lattice imaging
Detection Limit (ppm)	surface image	1,000	20,000	1000	defect imaging	lattice imaging
In-Depth Profiling Resolution	stereo microscopy	20 Å	20 Å	none	stereo microscopy	none
Time for Analysis	< 1 hour	< 1 hour	< 1 hour	< 1 hour	1-3 days	1-3 days
Comments	In-depth profiling achieved by angle-lap cross section	Profiling achieved by argon sputtering	Profiling achieved by argon sputtering	Wave-length & energy dispersive analysis	sample preparation requires specialized techniques and is time consuming	

## Review of modern characterization methods

Table Ic. X-ray probes

	Powder X-ray Diffraction (XRD)	Thin Film Analysis (Seeman-Bohlin)	Lang X-ray Topography (Lang)	Double Crystal Topography (DCT)	X-ray Fluorescence (XRF)	X-ray Photo-electron Spectroscopy (XPS,ESCA)
Depth Analyzed	10-50 $\mu\text{m}$	100 $\text{\AA}$ - 1 $\mu\text{m}$	500 $\mu\text{m}$	5-100 $\mu\text{m}$	1-3 $\mu\text{m}$	20 $\text{\AA}$
Diameter of Analysis Region	> 1 mm	1x5 mm	> 1 cm	> 1 cm	> 5 mm	5 mm
Detection Limit (atoms/cm <sup>3</sup> )	5x10 <sup>19</sup>	5x10 <sup>19</sup>	1x10 <sup>-3</sup> in $\Delta d/d$	1x10 <sup>-7</sup> in $\Delta d/d$	1x10 <sup>19</sup>	5x10 <sup>19</sup>
Detection Limit (ppm)	1000	1000	---	---	200	1000
In-depth Profiling Resolution	none	none	stereo topography	none	none	20 $\text{\AA}$
Time for Analysis	< 1 hour	2 hours	1 hour	4 hours	10 min	< 1 hour
Comments	sample cannot be amorphous	grazing incidence beam used	whole slice survey	whole slice survey	rapid & quantitative	In-depth profiling by argon sputtering

Table Id. Particle beams

	Rutherford Backscattering Spectroscopy (RBS)	Neutron Activation Analysis (NAA)	Ion Microscope (IMS,SIMS)	High Energy Ion Channeling	Charged Particle Activation Analysis (CPA)
Depth Analyzed	200 $\text{\AA}$ - 1 $\mu\text{m}$	1 $\mu\text{m}$	50 $\text{\AA}$	100 $\text{\AA}$	300 $\mu\text{m}$
Diameter of Analysis Region	2 mm	> 1 cm	> 5 mm	1 mm	5 mm
Detection Limit (atoms/cm <sup>3</sup> )	5x10 <sup>19</sup>	5x10 <sup>11</sup> - 5x10 <sup>18</sup>	5x10 <sup>15</sup> - 5x10 <sup>18</sup>	5x10 <sup>16</sup>	5x10 <sup>13</sup>
Detection Limit (ppm)	1000	0.00001 - 100	0.1 - 100	1.0	0.001
In-depth Profiling Resolution	200 $\text{\AA}$	1 $\mu\text{m}$	50 $\text{\AA}$	surface technique	25 $\mu\text{m}$
Time for Analysis	1 hour	2-5 days	1 hour	2 hours	2 hours
Comments	No standards needed	In-depth profiling by chemical etching	Spatial Resolution near 1 $\mu\text{m}$	crystal-line substrate required	In-depth profiling by chemical etching

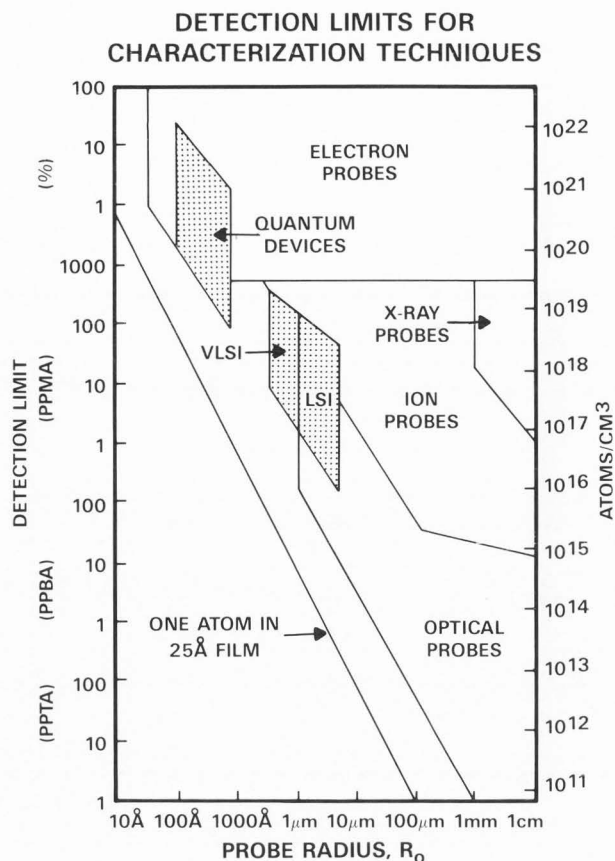


Fig. 1. Materials characterization techniques offer a choice between detection limit and analyzing spot size. The probing radiation must be selected according to the nature of the problem at hand.

band structure. Table 1 outlines some capabilities of common characterization techniques used in the semiconductor industry today.

### Applications

In applying characterization techniques information from one method complements another, and multiple analyses often resolve questions left unanswered by a single technique alone. In considering Figure 2, this can be appreciated by noting the complementary nature of the utility plots shown. A simple process flow has been adopted to illustrate how each probing radiation tends to specialize in the type of information it offers. For example, particle techniques which are sensitive to trace impurities and dopants clearly complement those methods employing beams of electrons for defect and surface definition. X-ray techniques specialize in crystalline imperfections and determination of composition. In the following, an example for each process step in the figure will be given to illustrate the inherent specializations of instrumentation available today. Existing inadequacies will then be discussed relative to new and evolving methods of characterization.

### Crystal Growth

Characterization for crystal growth is concerned with the iden-

tification of bulk impurities, dopants and the elucidation of defects and crystal damage (Dyer, 1983). Dopant and impurity atom levels normally below a part-per-million are best detected using those techniques which achieve ultrasensitivity at the expense of spatial resolution.

In neutron activation analysis (NAA), for example, the specimen is placed in a thermal neutron flux within the core of a nuclear reactor and radioactive nuclei are formed through nuclear reactions on stable isotopes (Keenan et al., 1985). The gamma radiation from their decay is measured and used to identify long lived nuclei (>2 day half-life) with sensitivities approaching 10<sup>11</sup> atoms/cm<sup>3</sup> (2 parts-per-trillion). This superb sensitivity is achieved at the expense of a large specimen volume, which is typically near 1 cm<sup>3</sup>. The region of analysis can be controlled by breaking or etching the specimen into smaller pieces.

Czochralski silicon contains oxygen which is introduced during crystal growth from dissolution of the quartz crystal crucible. Typical ingots contain 20 to 40 parts-per-million, with both radial and axial macroscopic variations. At temperatures where device processing occurs, the oxygen concentration is greater than its solubility in silicon, and precipitates form during cooling which cause strains and disruptions in the lattice (Keenan and Larrabee, 1983). The transmission electron micrograph in Figure 3, shows that these can form a highly efficient internal gettering network within the material for most metal contaminants.

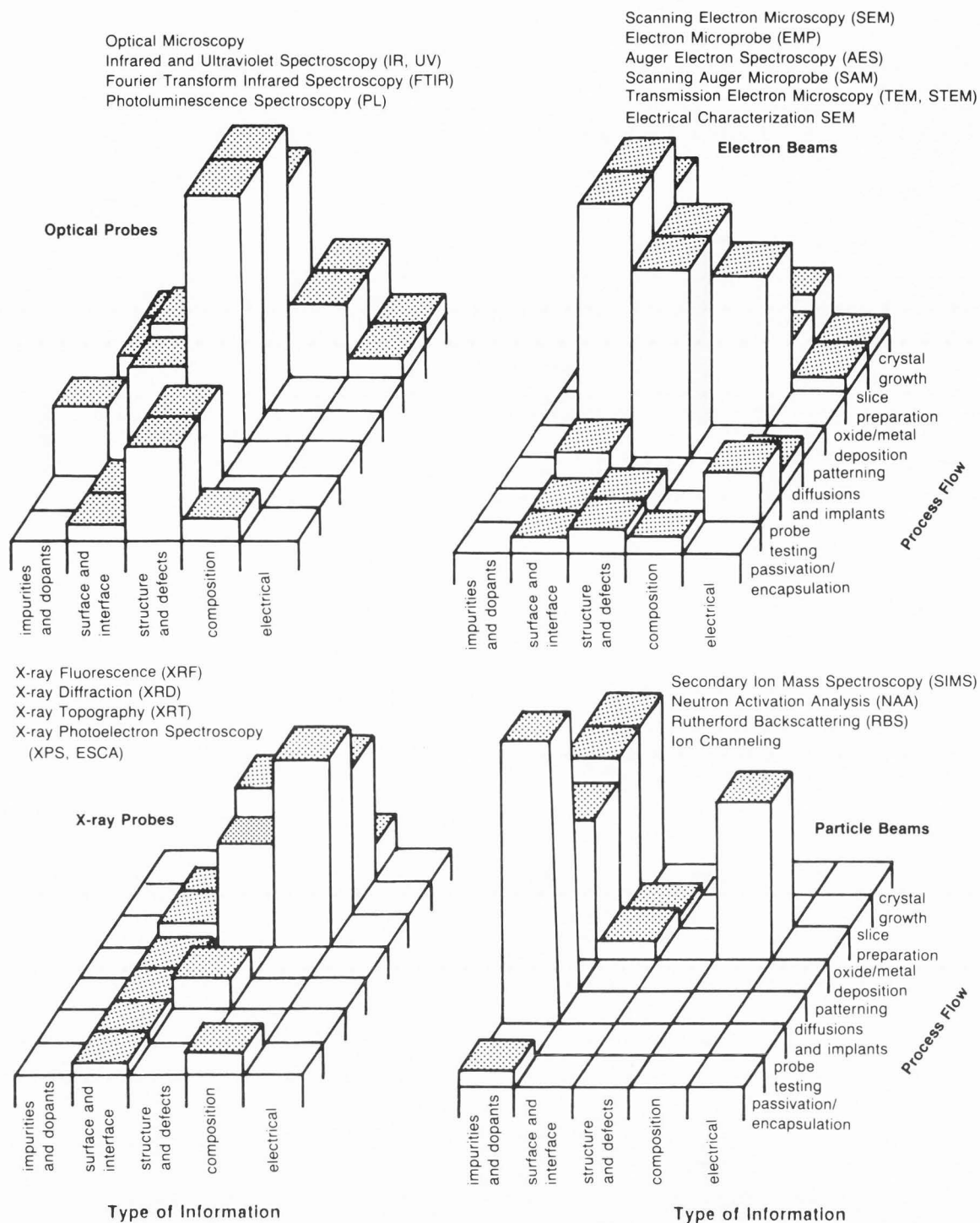
Infrared spectroscopy has found utility in characterizing dopant species (groups IIIA and VA) and determining the presence of carbon and oxygen in silicon (Stallhofer and Huber, 1983). Spectrometers that employ a Michelson interferometer as the dispersing element realize orders of magnitude advantage in sensitivity because the light otherwise lost in a narrow slit grating can be collected. The resulting diffraction information can be transformed by Fourier analysis to yield the desired spectrum and is the basis for Fourier transform infrared (FTIR) spectroscopy. The high sensitivity for thick samples (0.2–1 cm) and insensitivity to surface contamination are advantages for bulk analysis.

Correlations between impurity gettering sites and device performance are now well documented (Huff et al., 1983). The characterization of interstitial oxygen within bulk silicon is fundamental to this science, and FTIR has evolved as a choice method for its measurement. The influence of carbon on the precipitation behavior of oxygen is now being recognized, and its measurement is also largely dependent on FTIR. A two-phonon silicon lattice band at 610 cm<sup>-1</sup> overlaps the carbon absorbance and limits sensitivity for carbon to about 0.5 parts-per-million.

### Slice Preparation

Methods for the identification of dopant and impurity species in crystal ingots also apply to single slices, but many additional fabrication steps such as sawing, edge grind, polish and back-side damage require that specialized techniques be available for characterizing large and small defects induced by these mechanical processes. X-ray topography has recently emerged as a powerful monitor in this arena, being sensitive not only to macroscopic features such as flake chips, surface fractures, scratches, edge cracks and wafer warpage, but also to microscopic defects including stacking faults, dislocation loops, and slip.

## Review of modern characterization methods

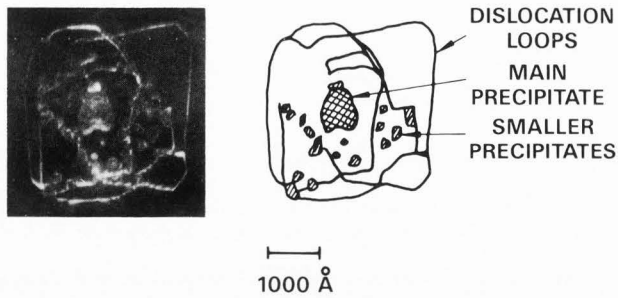


**Fig. 2.** These utility plots illustrate the importance of each probing radiation relative to process flow and the type of information available. The vertical axis represents frequency of use.

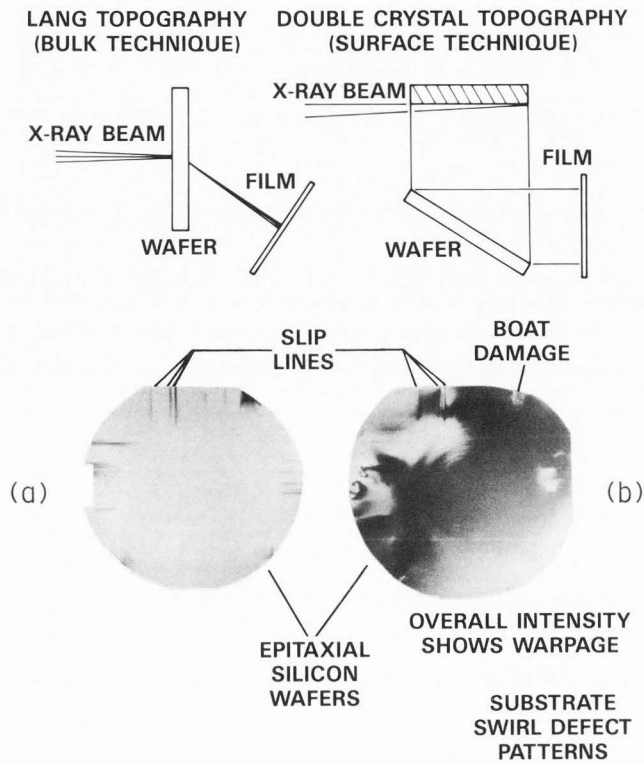
In Lang topography, a slit of x-rays is collimated onto the slice and the diffracted beam used to expose a recording film. In the presence of lattice imperfections, the intensity of the diffracted beam can be altered by distortions which act like microlenses to focus or defocus the otherwise diverging beam. Other mechanisms involving kinematic (Bragg's law) and dynamic (phase sen-

sitive) phenomena are also involved. Multiple slit exposures achieved by mechanical scanning can be used to form a wafer image which highlights defect structure, as shown in Figure 4(a). Subject to appropriate thermal cycling, the uniformity of oxygen precipitation within the bulk of the wafer can be readily detected.



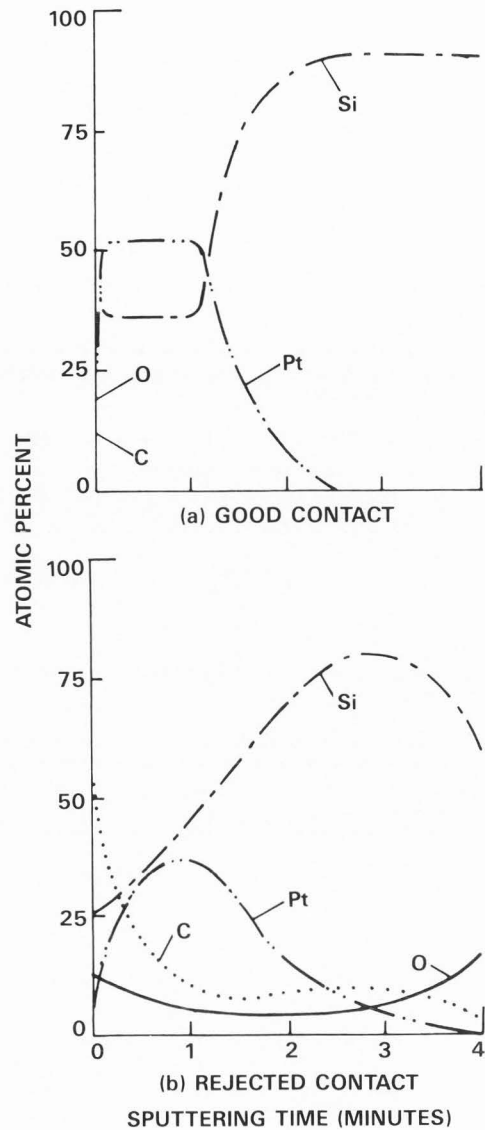


**Fig. 3.** Transmission electron microscopy was used to image this oxygen precipitate in silicon. Accompanying punched out dislocation loops can be seen which act as entrapment sites for metal impurities.



**Fig. 4.** Lang and double crystal x-ray topography have evolved as powerful imaging techniques for characterizing intrinsic and process induced defects in single wafers and epitaxial layers.

Double crystal topography achieves ultrasensitivity to lattice strains by employing a reference crystal which reduces divergence of the probing x-ray beam to less than 0.01 seconds of arc. Defect induced angular changes in the lattice, which normally would be obscured by divergence of the beam, can now be clearly resolved. Sensitivity of the technique is sufficient to detect wafer warpage defined by a one kilometer radius of curvature. The additional attribute of surface character (7-50  $\mu\text{m}$  depth) renders this an ideal technique for the study of deposited epitaxial films. One example is given in Figure 4(b), where evidence of boat damage, warpage, and ingrown defects from the substrate are evident.

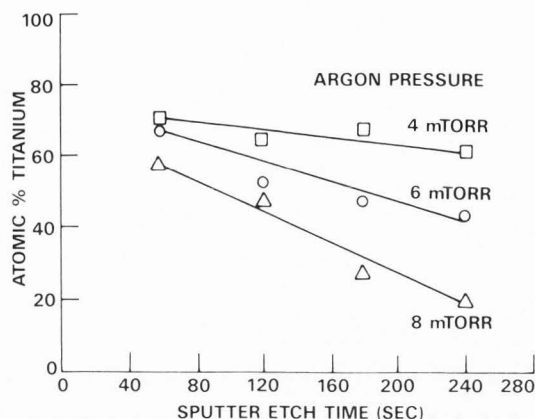


**Fig. 5.** Carbon from a contaminated substrate was found to permeate throughout micron sized PtSi diode windows used in low power Schottky devices. Poor stoichiometry and high carbon were responsible for a 50% change in barrier height.

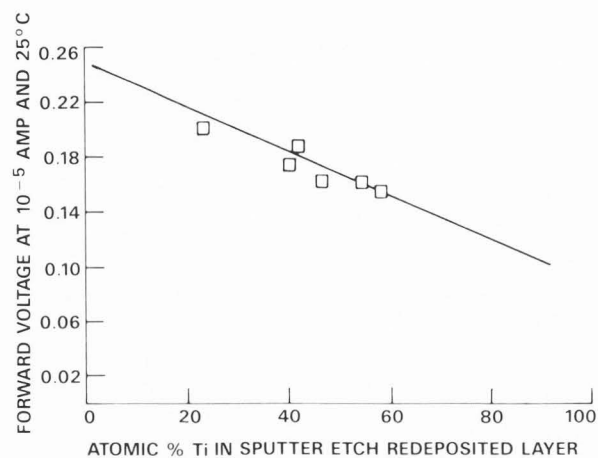
**Oxide/Metal Deposition**

The understanding of grain boundary diffusion, intermetallic migration and mixing, and mechanisms of metals contamination has relied heavily on the electron and particle beam based techniques which have depth monitoring capacity. It is known that C, O, and N concentrations less than a few atomic percent significantly alter the resistivity and stability of resistors, capacitors and active device junctions (Morabito, 1974). In the example of Figure 5, carbon from a contaminated silicon slice was found to permeate throughout 200 Å depositions of micron sized PtSi diode windows used for low power Schottky devices. Poor metal stoichiometry in addition to the carbon was responsible for a 50% change in barrier height. Small spot capacity and indepth profiling capability of the scanning Auger microprobe made it ideal for this application.

Metal contaminants are often associated with stainless steel



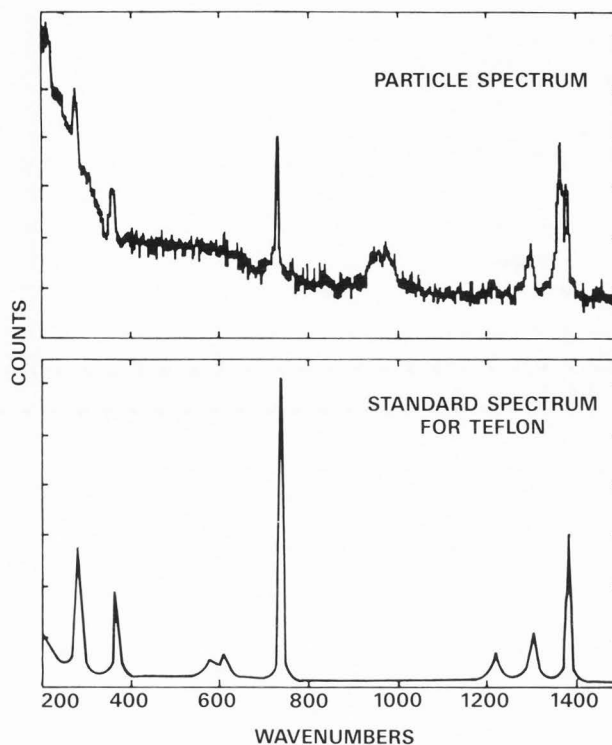
**Fig. 6a.** Rutherford backscatter channeling was used to demonstrate that the composition of an unexpected monolayer of TiW inadvertently deposited during a sputter clean operation depends on the argon pressure and the sputter time.



**Fig. 6b.** The forward voltage drop of Schottky diodes was found to depend strongly on composition of the layer.

and aluminum parts of the sputtering station. In one example, the surfaces of sputter-cleaned silicon wafers were characterized by high energy ion beam channeling with considerable success in explaining inconsistencies in the forward voltage drop for Schottky diodes in bipolar circuits. In ion beam channeling, the major axes of crystalline targets are aligned to an incident 3 million electron volt  $\text{He}^{++}$  ion beam, so that backscatter yields are reduced as the beam channels (Keenan, 1985). Deviations from gradual dechanneling offer a measure of the depth distribution of surface damage or contamination in the material.

It was found that a sputter cleaning step routinely incorporated the ambient argon gas into the silicon substrate and inadvertently deposited up to a monolayer of TiW metal. The source of the metal was a protective coating that was placed on the pallet that held the wafers. Surface analysis by channeling demonstrated that the composition of this first monolayer depends on the sputter time and the argon pressure for a given composition of protective coating, as shown in Figure 6(a). The comparison between electrical measurements and channeling shown in Figure 6(b) verified that the forward voltage drop is controlled largely



**Fig. 7.** A submicron speck examined in situ on a patterned wafer was identified as teflon in this spectrum from the Raman microprobe.

by the composition of the contaminant layer.

#### Patterning

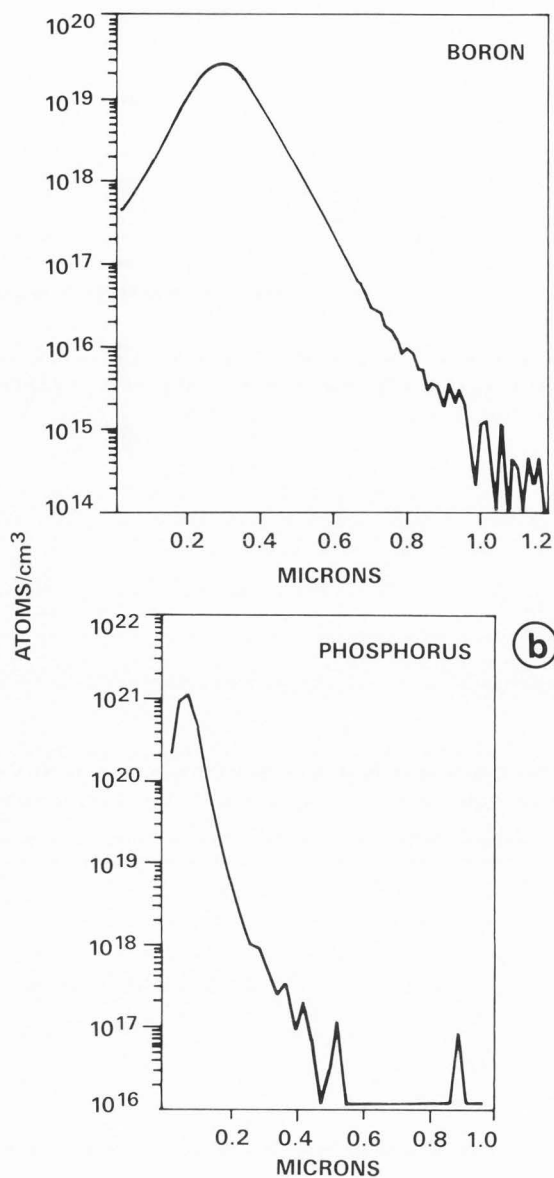
Techniques best suited for patterning diagnostics are normally those that have sufficiently high x-y spatial resolution to resolve individual circuit geometries. Those samples related to lithography involve organic resists or particulates from sources such as skin flakes, clothing lint, hair or makeup powder. These result in process problems which by comparison with material structure applications find little benefit from conventional electron and ion beam microscopies. One reason for this is that insulating organics are not able to adequately conduct away the charge that accumulates from these beams during the analysis. Infrared techniques avoid the charging problem and also yield information about molecular structure, but these are generally limited to larger specimens.

The Raman microprobe is a unique instrument that works well for the analysis of small organic contaminants (Needham and Ramsey, 1981). In this technique, the green or blue line (514.6 or 487.9 nanometer) from an argon laser is focused into a micron sized spot on the specimen and scattered light is collected by the same objective lens of the microscope and transferred into a spectrometer for analysis. The Raman vibrational modes excited by the light can be used as a fingerprint to identify the contaminant. For example, a submicron speck examined in situ on a patterned wafer was identified from the spectrum in Figure 7 as teflon and traced to a deteriorating acid bath support boat.

#### Diffusions and Implants

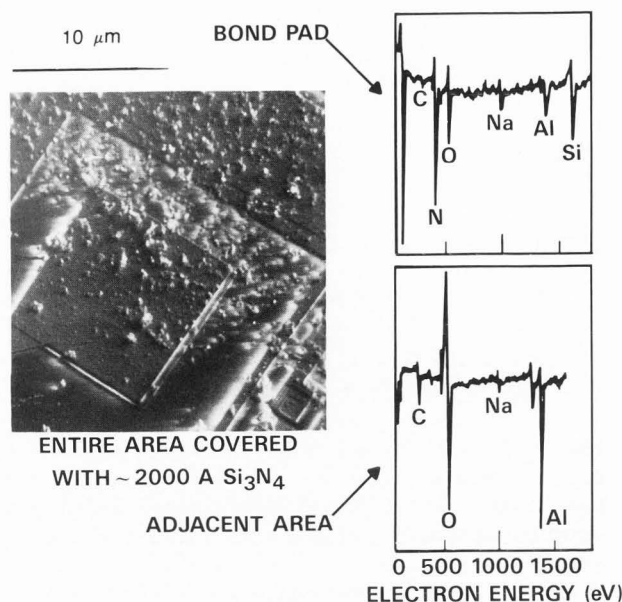
Secondary ion mass spectroscopy (SIMS) is one of the most useful tools for the characterization of diffusions and implants.





**Fig. 8.** Boron and phosphorus implant distributions in silicon can be measured in about an hour using the ion microscope. A mass interference between <sup>30</sup>SiH and <sup>31</sup>P reduces sensitivity to phosphorus.

This is because it combines a sensitivity adequate for parts-per-million analysis with depth profiling capability and near micron spatial resolution. It is fundamentally a depth profiling tool more than a bulk survey technique. There are variations in the way SIMS is implemented, but all of the methods employ an ion beam to systematically etch the specimen and release charged molecular fragments and atoms. These are collected and analyzed for charge-to-mass ratio. Simple configurations typically use an argon beam and quadrupole spectrometer. In more sophisticated systems, positive fragments are generated for analysis using a beam of O<sub>2</sub><sup>+</sup>, and negative fragments by using O<sup>-</sup> or Cs<sup>+</sup>. Modern spectrometers couple electrostatic and magnetic analyzers for optimum mass resolution (near 7000M/dm) and sensitivity (sub-parts-per-million for most elements). If a raster-



**Fig. 9.** Vias cut through a protective nitride overcoat on this linear circuit were found by Auger electron spectroscopy to be incompletely cleared. Loss of electrical contact and total bonding failure resulted.

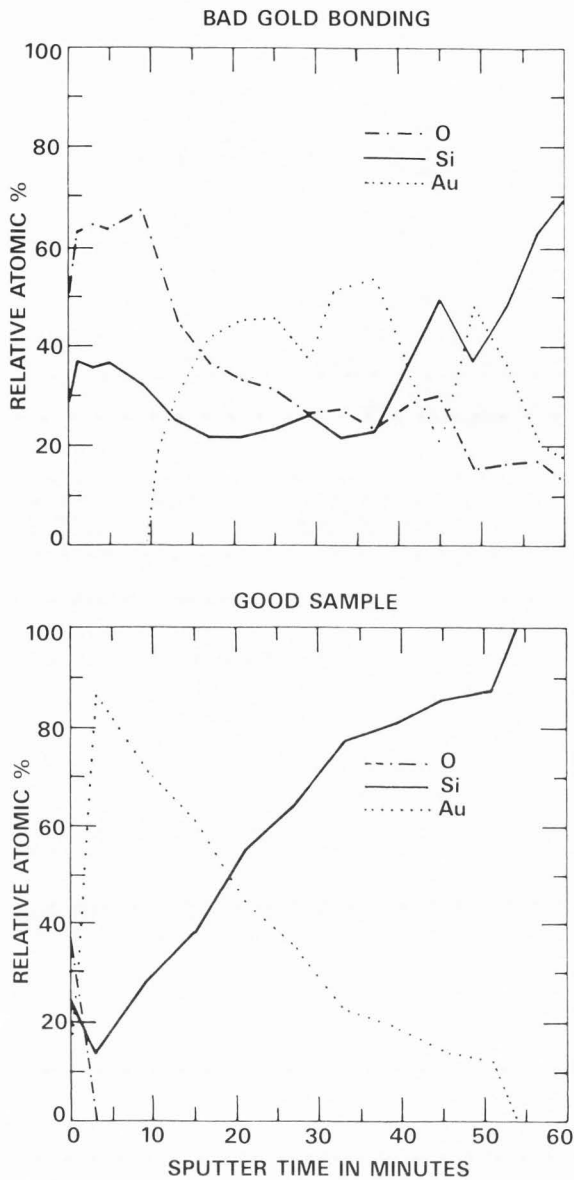
ing focused ion probe is used to achieve point-by-point resolution, the instrument is called an ion microprobe, while focusing optics analogous to the light microscope are the basis for the ion microscope.

Implants of boron and phosphorus in silicon are typically monitored by SIMS. It is straightforward to achieve 10<sup>15</sup> atoms/cm<sup>3</sup> detectability with boron profiles in silicon (Figure 8(a)). The detection of <sup>31</sup>P is complicated by the presence of the <sup>30</sup>SiH molecule which is of nearly equal mass. This requires that a high mass resolution analysis be performed at the expense of sensitivity, as shown in Figure 8(b). Modern methods for dissociating molecules to eliminate mass interferences are discussed later in this paper.

#### Probe Testing

Pressure contacts formed by metal tips during probing and the formation of thermo-compression and ultrasonic wire bonds all seek to achieve intimate contact with the bonding pads of chips to be tested. During the past decade, considerable activity has been focused on the description and solution of problems involving bonding surfaces and pads. Mechanisms of failure generally involve thin contamination layers, grain boundary diffusion phenomena, or variations in thickness of metal components. Most problems are traced in unclean systems that leave a thin layer of contamination between the bonding surfaces.

Auger electron spectroscopy (AES) has been instrumental in resolving problems with bonding, because it combines a high sensitivity to cleanup related elements such as carbon, oxygen, and nitrogen with the capability to inspect micron sized spots within the bond pad structure. Carbon in cleanup fluids and acid baths is common, and it is often detected by AES as residues of photoresist (Holloway and Bushmire, 1974). Metallic impurities in electrolyte solutions can codeposit in the plated metal and concentrate under subsequent temperature cycling at the bonding interface. Levels below 50 parts-per-million of Al,



**Fig. 10.** Using Auger profiles, chip bonding failure to a gold header was related to surface oxide formation caused by silicon migration. Adjustment of the anneal temperature used to form the Si/Au composition profile resolved the problem.

Ca, Ni, Fe, Cu, and Mg measured in plating baths by emission spectroscopy have been detected in the Auger spectra of bonding surfaces (McGuire et al., 1977). Migration of substrate metals such as Cu and Fe through thin protective Au layers can lead to surface oxidation and bond fracture. In the example of Figure 9, vias through a protective nitride overcoat on a linear circuit were found by AES to be incompletely cleared. The residual nitride was responsible for total bonding failure and loss of electrical contact.

#### Passivation and Encapsulation

Corrosion is a primary problem for plastic and glass encapsulated devices, and as complexity grows, high pin count pack-

ages must have low thermal and electrical impedances for high speed systems. Glass deposited by chemical vapor deposition is phosphorous doped to alleviate stresses that may result in cracks and also serve as a getter for alkaline ions. Its presence in humid environments can lead to phosphoric acid formation and attack on aluminum metallization within the chip.

In the absence of charging, Auger electron spectroscopy and electron microprobe analysis have been used to describe phosphorus distributions within these glasses. Electron microprobe analysis has considerable advantage over Auger spectroscopy for this application, because it detects only x-rays emitted from the volume of material excited by an impinging electron beam, and these are insensitive to charge accumulation within the glass. Silicon nitride is also used as a passivating layer, and problems with inconsistency of stoichiometry, oxygen content, and etch rate have been investigated by the two methods.

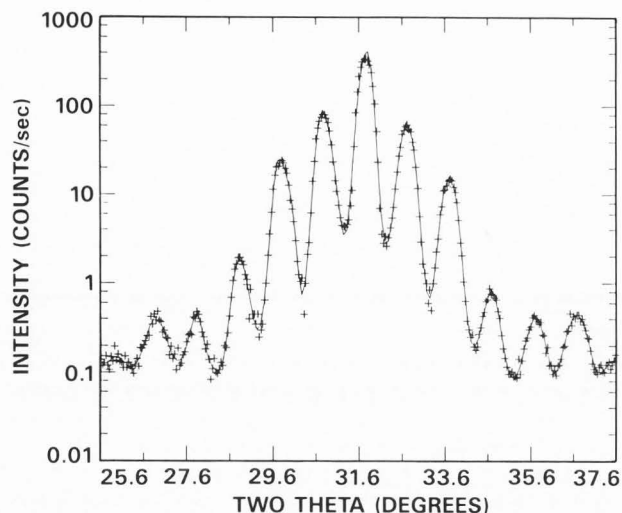
The problem illustrated in Figure 10 occurred when chip bonding to a gold header consistently failed. The backside of the silicon chip is preconditioned by sputter depositing 800 Å of gold, and then annealing at 300°C to form the graded composition shown by the Auger profile in Figure 10(a). It was found in Figure 10(b) that the diffusion of silicon between substrate and surface had resulted in formation of a dense surface oxide which was responsible for the bonding failure. The problem was traced to an excessive anneal temperature and was easily corrected.

#### Evolving Characterization Capabilities

The need for specialized techniques in problem solving applications is increasing as more stringent requirements evolve for purity of materials, control of doping levels, superior pattern registration, reduced geometrical design and particle control. For example, recent interest in heterostructures and superlattices has developed in the exploration of artificially structured materials. Emphasis has been placed not only on the development of a fundamental scientific understanding of atomic multilayered structures, but also on techniques of fabrication by molecular beam epitaxy (MBE) [Report on ASM, 1985]. Activities in this area include resonant tunneling in quantum wells and photon detection based on miniband transitions and direct gap behavior in Group IV superlattices. For II-VI compounds, the superlattice concept offers the possibility of a new generation of materials in which parameters such as bandgap and effective mass can be independently tuned. This technology holds great promise for the infrared device industry in the 8 to 14 micrometer spectral region where problems relating to tunneling and dark current exist. With group IV superlattices (i.e., Si and Ge), experimental research is seeking to produce direct bandgap materials with enhanced electron mobilities. The ability to characterize a single interface with atomic precision is now in demand to provide timely feedback for optimization of the MBE growth of such structures.

#### X-Ray Diffraction

One salient feature of superlattice structures is the periodicity that results from the preparation of alternate thin layers. Techniques of x-ray diffraction offer a rapid and nondestructive way to measure this periodicity, and more detailed inspections can yield additional information about elastic strain, dislocation density and terracing effects in the lattice (Segmuller et al., 1977). High precision instruments such as a four-circle x-ray diffractometer with monochromator or a double-crystal topography



**Fig. 11.** Satellite peaks about the (002) reflection were recorded from an MBE grown AlAs/GaAs superlattice with an automated four-circle diffractometer and used to measure the new artificial periodicity as  $93\text{\AA}$ .

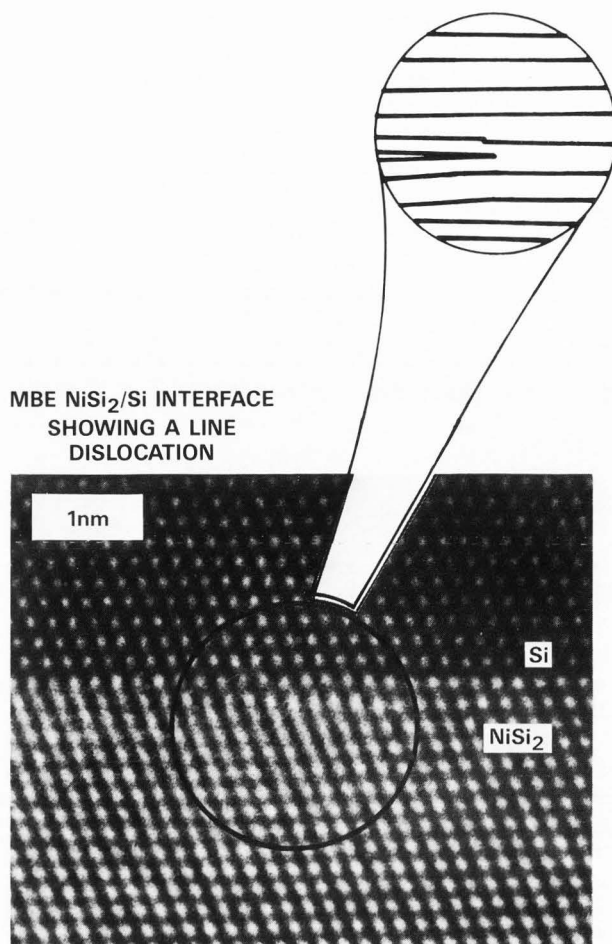
camera are typically used for these measurements. The example in Figure 11 is a line scan taken through the (002) reflection of an AlAs/GaAs modulated superlattice grown by MBE. The periodic oscillations which form satellites to the main peak were used to quickly and accurately establish superimposed periodicity of the structure as  $93\text{\AA}$ , which is in good agreement with  $95\text{\AA}$  expected from the growth conditions.

#### High Voltage Transmission Electron Microscopy (HVTEM)

In recent years, workers with HVTEM have succeeded in achieving spectacular images of MBE grown superlattices with single atom resolution (Jeng et al., 1985). Today, commercial instruments offer up to 400 kilovolt electron source capability, and pioneering laboratories in the U.K., U.S., and Japan continue to experiment with one million volt machines. One example is shown in Figure 12 which reveals a line defect in the lattice image of a  $\text{NiSi}_2/\text{Si}$  interface prepared by MBE. It is natural to think of these spots as individual atoms at the surface, but in reality they are formed by accepting diffracted electron beams that penetrate through the specimen. It is more correct to think of them as stacked columns of atoms, extending throughout the thickness of the specimen. The greatest challenge in applications remains in the preparation of thin, durable and intact specimens.

#### Tunneling Microscopy

A new technique capable of single atom detection called scanning tunneling microscopy has recently been developed at IBM's research laboratory in Zurich (Binnig and Rohrer, 1985). It can simultaneously resolve features of the outermost monolayer of a specimen with differences in vertical position as small as  $0.1\text{\AA}$ , and horizontal separations down to  $2\text{\AA}$ . The phenomenon that makes the approach possible is the vacuum electron tunneling that occurs between individual atoms on the surface and a pointed metal tip that can be positioned arbitrarily close. The technology is focusing on ingenious methods for controlling the probe's position and on fabrication techniques for achieving single atom emission points from the tip. This field is now ripe for new developments and applications.



**Fig. 12.** High voltage transmission electron microscopy was used to delineate this line dislocation defect near the interface of a  $\text{NiSi}_2/\text{Si}$  structure grown by molecular beam epitaxy. The image is reproduced courtesy of Dr. E. Hall of General Electric Corporation.

#### Single Atom Detection

Techniques capable of single atom imaging pose interesting new questions about detectability and the use of equation (1). This was mentioned earlier to relate signal-to-noise (S/N) and the radius ( $R_0$ ) of the probing radiation. The fundamental assumption is that the number of atoms detected is large and the probability for detection of a single atom small, and this is the basis for Poisson statistics which describe the majority of analytical techniques in use today.

For single atom detection, the conditions are exactly reversed. The situation can be appreciated by considering the example in Figure 13. As  $R_0$  decreases, there is ultimately an analysis volume which includes only several of the species atoms of interest. The technique of analysis must have near unity probability for detection of a single atom to be successful, because the number of atoms is no longer large. For even smaller probes, the volume may contain no species atoms at all. In addition, the analyst is now confronted with a severe sampling problem in selecting which atoms are appropriate for the analysis. The more general binomial distribution can be used to describe this case, and some results of its application are summarized in Table 2.

**Table 2.** For single atoms, conventional Poisson statistics which govern detectability break down. Application of the more general binomial distribution leads to the intuitive conclusion that the probability of detection for single atoms must be near unity for any technique to be successful.

	$S/N = \sqrt{Np/(1-p)}$	
	N Determined By:	S/N Determined By:
Poisson Distribution (N large)	$\rho \pi r_0^2 z_0$	$r_0 \sqrt{z_0}$
Binomial Distribution (N small)	$\sum \delta_i (r_i < r_0) \delta_i (z_i < z_0)$	$\sqrt{p/(1-p)}$

S/N	signal-to-noise
N	number of atoms in detectable volume
p	probability of detecting a single atom
$r_0$	probe radius
$z_0$	probe depth
$\rho$	atom density
$\delta_i(x < y)$	= 1 when $x < y$ , otherwise = 0

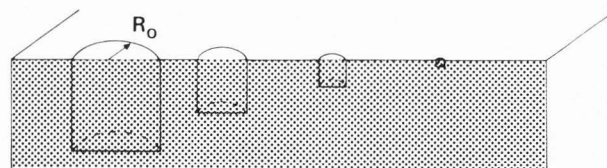
**Parts-per-Trillion Methods**

Methods of analysis that function between single atom detection and parts-per-million capability offer a reasonable compromise with the sampling problem, and remain essential to the development of semiconductor technology. They are approaching that transition region where Poisson statistics become inadequate for the description of nonuniform dopants and clusters of atoms. Generally, ion beams are evolving as the optimum probe in this region but other techniques such as neutron activation analysis and photoluminescence spectroscopy have been of value in specialized applications.

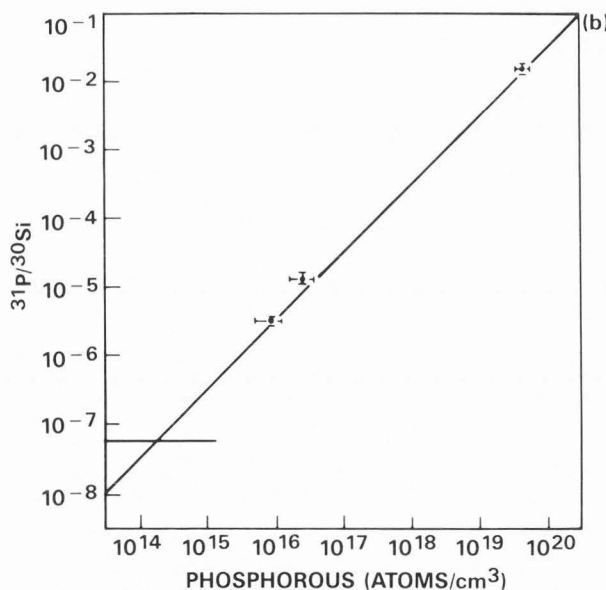
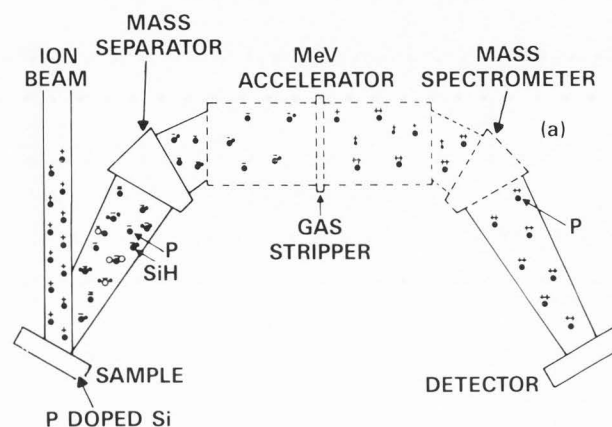
Today, secondary ion mass spectroscopy (SIMS) is the most widely used method for trace element analysis because as previously mentioned, it strikes a useful compromise between spatial resolution (about a micrometer) and detectability (near a part-per-million) for most of the elements in the periodic table. Its primary limitation originates from a mass interference problem which arises when two species such as  $^{30}\text{SiH}$  and  $^{31}\text{P}$ , or  $^{28}\text{Si}_2$  and  $^{56}\text{Fe}$  have the same mass number.

**SuperSIMS**

To resolve the mass interference problem, a promising new technique based on an older technology designed for ultrasensitive radioisotope dating is now being developed (Anthony et al., 1985). This is an accelerator-based mass spectroscopy we call "SuperSIMS," which couples the conventional SIMS machine to a high energy particle accelerator, as illustrated in Figure 14(a). Sputtered molecular fragments are accelerated to several million electron volts, which results in repulsion of nuclei by stripping two or more electrons from the constituent atoms. Repulsion breaks the fragments into single atoms that can be detected individually. At the million volt energies employed, detection of single atoms from the accelerator can be realized using established nuclear particle counters and techniques. Parts-per-billion sensitivity has already been achieved for phosphorus in silicon (Figure 14(b)), and expectations for achieving parts-per-trillion are realistic.



**Fig. 13.** As the radius ( $R_0$ ) of the probing radiation decreases, a point will be reached in which no atoms of the species of interest lie within the analyzed volume.

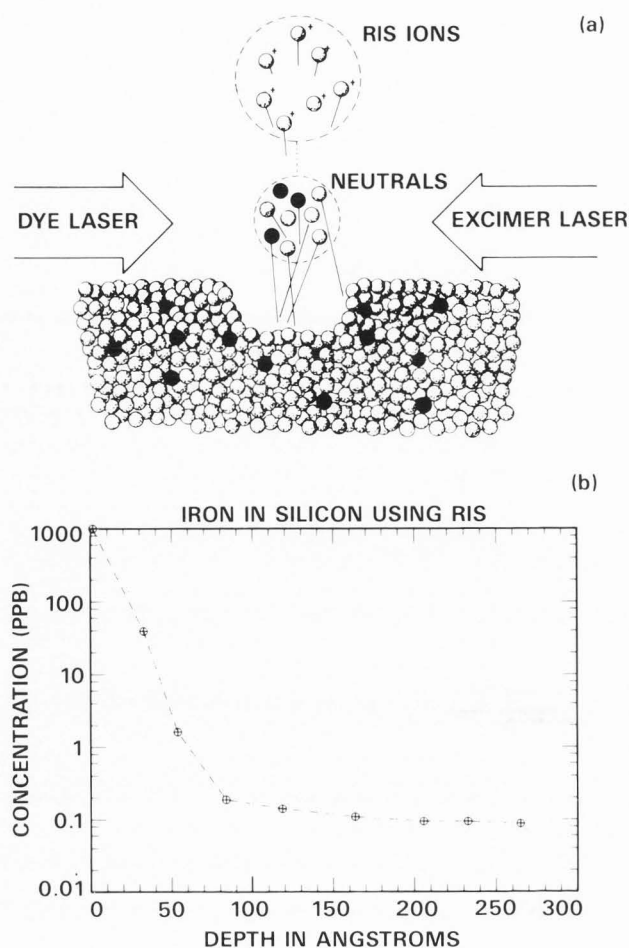


**Fig. 14.** In (a), "SuperSIMS" couples the conventional SIMS machine to a high energy particle accelerator to break apart ambiguous mass fragments. Parts-per-billion sensitivity shown in (b) has been achieved for detecting phosphorus in silicon. The horizontal line represents background level for the instrument.

**Resonance Ionization Spectroscopy**

Other activities are ongoing with a related method based on the selective excitation by laser light of sputtered atomic species (Iversen, 1984). This technique has been designated by a variety of acronyms, and the one adopted here is resonance ionization spectroscopy (RIS). As an ion beam impinges on the sample,





**Fig. 15.** The resonance ionization spectroscopy (RIS) technique offers ultrasensitivity by selectively ionizing from a cloud of neutral atoms only those that are of interest. Iron in silicon at the part-per-trillion level has been detected.

sputtered particles form a small cloud above the surface, as illustrated in Figure 15(a). Any secondary ions generated during the process are removed by momentarily applying a voltage to the sample, leaving a gas cloud consisting entirely of neutral particles. These are flooded with laser light of specific wavelength to selectively ionize the single element of interest. Because neutral particles account for more than 90 percent of the total sputtering yield, and selective ionization by laser light permits species discrimination without the intensity loss of a mass spectrometer, it is possible to realize as much as four orders of magnitude increase in sensitivity with RIS relative to conventional SIMS. Significant progress has been made in realizing parts-per-trillion sensitivity for Fe using this technique, as shown in Figure 15(b).

#### Photoluminescence Spectroscopy

In photoluminescence spectroscopy (PL), a population inversion of electronic excited states is created by visible laser light stimulation, and emissions resulting from relaxation to the ground state are analyzed. This is fundamentally an electrical characterization technique, because it senses band structure that

gives rise to the detected electronic transitions. A review of the method has been given (Smith, 1981) and applications for the determination of dopants in silicon can be found in the literature (Tajima, 1978). When coupled with the sensitivity advantage of the Michelson interferometer detection scheme previously discussed for FTIR, the measurement is incredibly sensitive. Trace levels of P, B and As can be quantitatively measured in silicon in the sub-part-per trillion range ( $<10^{10}$  atoms/cm<sup>3</sup>), and applications readily extend to impurities in direct gap III-V and II-VI alloy semiconductor materials. The shortcoming of PL lies in the limited number of elements amenable for analysis.

MATERIALS CHARACTERIZATION TECHNOLOGIES	
DEVELOPMENTS FROM 1975-85	NEW AREAS OF ACTIVITY
EDS X-RAY SPECTROMETERS	SUPERLATTICE CHARACTERIZATION
AUGER ELECTRON SPECTROSCOPY	MULTI-CHANNEL DETECTORS
SCANNING AUGER MICROSCOPY	ENHANCED RAMAN SPECTROSCOPY
SCANNING TEM (STEM)	THIN FILM X-RAY DIFFRACTION
RUTHERFORD BACKSCATTERING	TUNNELING MICROSCOPY
FOURIER TRANSFORM PL	CHARGED PARTICLE ACTIVATION
LANG X-RAY TOPOGRAPHY	EXPERT SYSTEM INTERPRETATION
DOUBLE-CRYSTAL TOPOGRAPHY	TABLE-TOP SYNCHROTRON
LATTICE IMAGING TEM	X-RAY LASER

gives rise to the detected electronic transitions. A review of the method has been given (Smith, 1981) and applications for the determination of dopants in silicon can be found in the literature (Tajima, 1978). When coupled with the sensitivity advantage of the Michelson interferometer detection scheme previously discussed for FTIR, the measurement is incredibly sensitive. Trace levels of P, B and As can be quantitatively measured in silicon in the sub-part-per trillion range ( $<10^{10}$  atoms/cm<sup>3</sup>), and applications readily extend to impurities in direct gap III-V and II-VI alloy semiconductor materials. The shortcoming of PL lies in the limited number of elements amenable for analysis.

#### Future Prospects

Many of the techniques of characterization we know today have evolved over the last decade from improvements in technologies, such as low noise electronic circuits, computer automation and ultrahigh vacuum science. From the previous examples, we see these trends continuing, and it is reasonable to expect that future breakthroughs will continue to happen. Table 3 outlines some areas where researchers are currently active and fertile ground lies for new methods of characterization.

It is clear that over the next decade, linewidths in very large scale integrated (VLSI) circuits will continue to shrink toward 0.5 micrometer to achieve higher computing power and speed per chip. The lithography required to fabricate these patterns is pushing optical systems to their diffraction limit (slightly below 1 micron) and stimulating ingenious processing schemes to overcome evolving problems with linewidth control, registration accuracy, parasitic resistance and capacitance, particle induced upsets and hot electron effects (Tasch, 1983). Increased demands on crystal purity slice preparation and metal/oxide depositions have already inched beyond capabilities for adequate characterization. These technologies once again are stimulating the synergistic partnership between materials characterization and device development.

## Review of modern characterization methods

### References

- Anthony JM, Donahue DJ, Jull AJT, Zabel TH. (1985). Detection of Semiconductor Dopants using Accelerator Mass Spectrometry. *Nuc. Instr. Method. B*, **11**, 498-500.
- Binnig G, Rohrer H. (1985). The Scanning Tunneling Microscope. *Scientific American*, August, 50-56.
- Dyer LR. (1983). Fracture Tracing in Silicon Wafers. *Electrochem. Soc. Ext. Abstr.* **83-2**, 553.
- Holloway PH, Bushmire DW. (1974). Detection by Auger Electron Spectroscopy and Removal by Ozonization of Photoresist Residues. *Proc. IEEE Rel. Phys. Soc.*, 12th, Las Vegas, Nevada, 180-186.
- Huff HR, Schaake HF, Robinson JT, Baber SC, Wong D. (1983). Some Observations on Oxygen Precipitation/Gettering in Device Processed Czochralski Silicon. *J. Electrochem. Soc.*, **130**, 1551-1555.
- Iversen WR. (1984). Laser Vastly Improves Iron-Impurity Detection. *Electronics Week*, December, 22-24.
- Jeng SJ, Wayman CM, Coleman JJ, Costrini G. (1985). Interface Characteristics of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As Superlattices Grown by MOCVD. *Materials Letters*, **3**, 89-92.
- Keenan JA. (1985). The Characterization of Semiconductor Materials by Backscattering Spectroscopy. *Nucl. Instrum. and Meth.*, **B10/11**, 583-587.
- Keenan JA, Gnade BE, White JB. (1985). Instrumental Neutron Activation Analysis of Processed Silicon. *J. Electrochem. Soc.*, **132**, 2232-2236.
- Keenan JA, Larrabee GB. (1983). Characterization of Silicon Materials for VLSI. *VLSI Electronics: Microstructure Science*, N. Einspurch (Ed.), Academic Press, Vol. 6, 1-72.
- McGuire GE, Jones JV, Dowell HJ. (1977). The Auger Analysis of Contaminants that Influence the Thermocompression Bonding of Gold. *Thin Solid Films*, **45**, 59-68.
- Morabito JM. (1974). Quantitative Analysis of Light Elements in Sputtered Tantalum Films by AES and SIMS. *Anal. Chem.*, **46**, 189-196.
- Needham CD, Ramsey JN. (1981). Application of Raman Microprobe Analysis to Semiconductor Materials and Problems. *Semicond. Int.*, March, 75-85.
- Report on Artificially Structured Materials (1985), National Academy Press, Washington, D.C., Chapter V, 85-109.
- Segmuller A, Krishna P, Esaki L. (1977). X-ray Diffraction Study of a One-Dimensional GaAs-AlAs Superlattice. *J. Appl. Cryst.*, **10**, 1-6.
- Smith KK. (1981). Photoluminescence of Semiconductor Materials. *Thin Solid Films*, **84**, 171-182.
- Stallhofer P, Huber D. (1983). Oxygen and Carbon Measurements on Silicon Slices by the IR Method. *Solid State Tech.*, Aug., 233-237.
- Tajima M. (1978). Determination of Boron and Phosphorus Concentration in Silicon by Photoluminescence Analysis. *Appl. Phys. Lett.*, **32**, 719-721.
- Tasch AF. (1983). Metal Oxide Semiconductor Technology Scaling Issues and their Relation to Submicron Lithography. *Optical Engineering*, **22**, 176-180.

### Discussion with Reviewers

**E.R. Levin:** Are not X-ray diffraction and HVTEM both already well known? It is the greater stringency of advanced chip development criteria that has brought better utilization of these methods than was realized formerly.

**Author:** I agree with this point, however, some of the more exotic x-ray techniques are not well known in the semiconductor industry. These include the double (and even triple) crystal topographies, Gandolfi techniques for small particle analysis, and grazing incidence methods for x-ray fluorescence, surface roughness or thin film measurements.

**E.R. Levin:** What methods other than vacuum tunneling microscopy are in prospect for single atom detection?

**Author:** This is the best example I know. Of course, one precursor technology to the tunneling development is field emission microscopy, which is capable of single atom imaging. Utility of this method for semiconductor applications is severely restricted by the number of materials that can be used to fabricate a stable emission tip. TEM lattice imaging does not directly probe single atoms, but the spatial separation between diffraction planes imaged by the technique is of Angstrom dimensions and information about periodic atomic arrangements can be obtained. Also, sensitivity for single atom events using the nuclear detection schemes mentioned with respect to SuperSIMS has been known for some time.

**E.R. Levin:** What methods can achieve part-per-trillion detectivity?

**Author:** The text specifically mentions RIS (Figure 15) and photoluminescence spectroscopy. Until now, SuperSIMS has been limited by purity of the ion source, which for Figure 14(b) was totally unfiltered. We fully expect sensitivity of the method to reach part-per-trillion capability when appropriate mass spectrometers are employed (as with ion microprobe instruments today) at the source.

**E.R. Levin:** Have you not overlooked the important role of the SEM and electron microprobe (EMP)?

**Author:** There is no intent to minimize the important role of these workhorse instruments to the semiconductor industry. They were omitted from discussion because references to their function and utility are widely available throughout the SEM journal. Optical microscopy and techniques of electrical characterization were likewise left out to reduce length of the review.

**G.E. McGuire:** Do not a number of XPS vendors quote diameter of analysis spot down to 150 $\mu$ m, especially with x-ray monochrometers?

**Author:** This is correct. One vendor now advertises this as well as a 128 multichannel detection scheme for improved data acquisition rate. Others offer competitive products which need to be evaluated in light of the intended analysis workstation and requirements. XPS instrument development is rapidly changing, and the technology is ripe for continued improvements.



**S. Thomas:** Recognizing that PtSi is altered in composition by ion bombardment, how did the author quantify the composition in Figure 5(a)? Please explain the apparent increase in oxygen concentration and decrease in silicon below platinum. How does the author conclude that carbon was responsible for 50% reduction in barrier height considering that the barrier height is a property of the metal/silicon interface?

**Author:** The quantification was achieved by the conventional method of normalizing the sum of all elements detected to 100%. Thus when Si decreases at the end of the profile it is because the oxygen value has increased. Reasons for the increase are not clear, but argon ion beam mixing could be responsible. The etch rate employed was 40 Å/min (3 keV at  $5 \times 10^{-6}$  amp/cm<sup>2</sup>). The problem was traced to cleanup contamination and resolved when it was eliminated.

The barrier height difference of 50% was found from direct electrical tests performed during manufacture. It is reported that thin carbon or oxygen layers sandwiched between metal and silicon provide a high trap density medium where stored charge can alter the barrier and lead to lower breakdown voltage (Nicollian EH, Schwartz B, Coleman DJ, Ryder RM, and Brews JR (1976) Influence of a thin oxide layer between metal and semiconductor on schottky diode behavior, *J. Vac. Sci. Technol.* **13**, 873).

**S. Thomas:** In Figure 9 the suggestion is made that the particulate residue is incompletely cleared Si<sub>3</sub>N<sub>4</sub>. Similar residue is seen outside the Al pad also. Please explain. Is the Na signal in the Auger spectrum typical of an IC surface?

**Author:** The particulates do in fact have similar composition to the nitride, and contain no carbon. They could be inorganic complexes which have nucleated in the presence of some contaminant, such as the sodium you mentioned. Sodium in the spectrum is seen occasionally on IC surfaces by scanning Auger spectroscopy, but more often it is necessary to use higher sensitivity techniques such as SIMS or neutron activation analysis to detect its presence.

**S. Thomas:** The author states that in the electron microprobe x-rays emitted by an impinging electron beam are insensitive to charge accumulation within the glass. The primary electron beam can indeed be altered by charge accumulation in the glass with the concomitant effect on x-rays.

**Author:** In extreme cases, bizarre effects in glasses can indeed be observed in the SEM and electron microprobe (cf. Shaffner TJ and Hearle JWS. (1976). Recent advances in understanding specimen charging, *Scanning Electron Microsc.* 1976; 1:61-82). In many instances the latter can tolerate considerably more charge buildup than other methods such as AES, SAM, or SIMS.

**S. Thomas:** One of the real challenges an analyst faces in all these characterization efforts using sophisticated tools, is to correlate the apparent material differences with the observed electrical properties. This correlation is not always obvious in today's complex IC's. In the final analysis, it is the electrical properties which are of more interest to the device engineer. Please comment.

**Author:** Both electrical and optical techniques are commonly used during and after device manufacture to provide real-time feedback and determine criteria for releasing the product. It is when these tests fail that the more sophisticated ones come into play. For example, poor refresh time in a dDRAM is best detected by electrical measurement, but knowledge that the particular contaminant is copper must be provided by more sophisticated follow-up methods. At this point, the SIMS or neutron activation analysis of copper becomes of more interest to the engineer because it provides a clue for correcting the problem.