

Microanalysis of Materials by Backscattering Spectrometry

New campaigns for a veteran technique.

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After its successful soft landing on the moon on 9 September 1967, Surveyor 5 transmitted back to earth signals which contained the first factual information on the chemical composition of the lunar soil. The data were obtained from the "alpha-scattering experiment" performed by a relatively simple instrument placed on the lunar soil. A radioactive source emitted alpha particles which were directed at the lunar surface. The particles were then scattered back by collisions with the constituent atoms of the lunar material and counted by suitably positioned, energy-sensitive detectors. From such measurements one can determine the mass of the collision partner and therefore identify the elements present in the soil (1, 2). These backscattering analyses agree remarkably well with the chemical analyses later made on samples of moon rocks returned to earth by the Apollo 11 and Apollo 12 missions (3).

The Surveyor experiment was the first widely publicized application of a backscattering analysis; yet the method as such was known to nuclear physicists almost 20 years ago and has since been a stock-in-trade item of their techniques for recognizing target contaminants (4). However, applications

of this same method to problems of "nonnuclear" interest have been virtually nonexistent for a decade following an isolated analysis of smog (5) and a little-known analysis of the bore surfaces of gun barrels (6). In the late 1960's preliminary studies showed that mineral analysis by this method was feasible (7). Tuross and Wilhelmi derived the thickness of elemental thin films from backscattering spectra obtained with light ions and also analyzed thick compound targets (8). Experiments with thin films and compounds were reported by Peisach and Poole (9). In a review article on surface microanalysis Mackintosh and Davies pointed out some of the advantages that channeling effects bring to backscattering from single-crystal specimens (10). These contributions demonstrated that the method is well suited to problems of material analysis. Practical results are now being obtained, with low-energy accelerators as sources of particles, in metallurgy, semiconductor processing, thin insulating and magnetic film technology, environmental pollution, and other areas as well.

In principle, this technique allows us, first, to determine the masses of the elements in the target, and, second, to map the distribution of mass in depth, over distances from 100 angstroms to a few microns from the surface. It thus constitutes a mass-sensitive depth microscopy. Third, the tech-

nique is also sensitive to crystalline structure. It is this simultaneous response to three distinct physical properties of the target, namely, the *mass* of the constituents, their *depth distribution*, and the *crystalline structure*, which makes backscattering such a versatile and valuable complement to established methods such as activation analysis, chemical microanalysis, x-ray fluorescence, and the like.

Practical consequences have already followed. It proved possible to define the conditions for growing oxide and nitride layers used in manufacturing integrated circuits, a result which would have been difficult to accomplish so readily by any other known analytical technique. Backscattering methods are being used to measure the penetration of printing inks into paper, as part of a research program aimed at improving paper quality and reducing ink wastage. Backscattering techniques have obvious relevance to the study of natural oxidation processes such as corrosion. They have also been used to detect the presence of impurity atoms within host crystal lattices, to identify them, to map their distribution in depth, and to establish the degree of substitution on regular lattice sites.

Thus far, backscattering has been applied most extensively to the analysis of ion-implanted semiconductors. This application now forms a familiar part of the literature (11, 12) on ion implantation in silicon. The development of backscattering as an analytical tool is being accomplished by cooperation of groups in Europe, Canada, and the United States. The combined experience with different accelerators and experimental methods employed in each laboratory provides good insight into the advantages and limitations of the technique. To illustrate the versatility of backscattering microscopy, the examples we present here have been chosen outside of the field of ion implantation, and, for convenience, most have been selected from work done at the California Institute of Technology. All these results were obtained with

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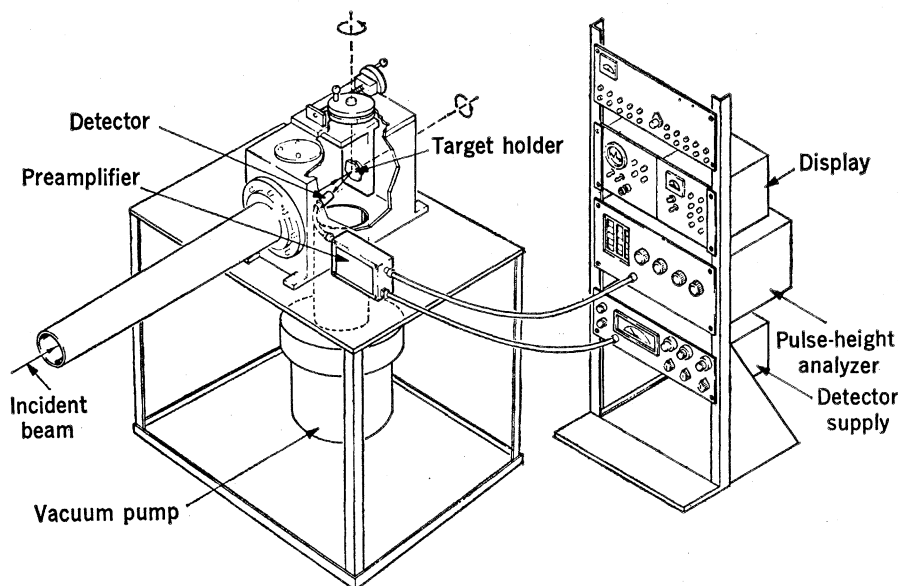


Fig. 1. Layout of a backscattering system. An accelerator (not shown) generates an atomic beam of high energy incident on the left. It impinges on the target placed in the high-vacuum chamber. Some atoms of the beam are scattered back. Their energies are analyzed by the detector, and the detector signal is magnified and reshaped in the preamplifier. The electronic equipment in the rack provides power to the detector and preamplifier, and stores the data generated by the detector in the form of backscattering spectra.

helium ions as projectiles in the energy range from 1 to 3 million electron volts. In many cases, this range represents a region of optimum overall performance in terms of mass resolution, depth resolution, and accessible depth.

Experimental Arrangement

Backscattering analysis is straightforward. Furthermore, every component in the system is common to most nuclear accelerator laboratories. The apparatus, shown schematically in Fig.

1, consists of an evacuated chamber which contains both the target and the detector. The solid-state detector produces signals whose amplitudes are proportional to the energy of each backscattered particle within its field of view. A preamplifier and a pulse-height analyzer amplify and convert the data which are either displayed on a screen, photographed and printed, or punched out for further handling by a computer. A particle accelerator (not shown in Fig. 1) generates the collimated beam. Crude spectra may be obtained in a few minutes of exposure;

typical runs last 15 to 30 minutes. One system for backscattering analysis can thus simultaneously fulfill the needs of many investigators.

Mass Analysis

One of the three salient features of the tool is its ability to distinguish the atomic masses of elements present in a target. Let us see how this is accomplished in the case of a very thin target composed of several kinds of atoms. When a flux of monoenergetic helium ions impinges upon this target, a very few helium particles collide with these atoms and will be scattered back by the electrostatic Coulomb repulsion of the atomic nuclei. The energy of the helium particle after such an elastic scattering event is smaller than its initial energy E_0 but is proportional to it through a factor K , which is given by

$$K = \left(\frac{M - m}{M + m} \right)^2 = 1 - \frac{4mM}{(M + m)^2} \quad (1)$$

Here m is the mass of the analyzing (helium) particle, and M is the mass of the target atom. For heavy target masses (M larger than about $10m$) the energy shift is nearly equal to $4(m/M)E_0$. In Eq. 1 it is assumed that the ion is reflected back exactly through 180° . For scattering angles smaller than this, a greater fraction of the incident energy is carried away by the backscattered particle. The backscattering angle is usually chosen to be as large as possible, so as to give the greatest energy difference, that is, the highest dispersion in the mass scale. Target atoms of mass equal to or less than the projectile mass ($M \leq m$) cannot generate backscattering spectra.

Figure 2 shows the result of a backscattering experiment performed with a thin, evaporated target containing approximately equal numbers of copper, silver, and gold atoms. Figure 2 shows a plot of the number of helium ions, backscattered through 164° , as a function of their energy. In accordance with the dependence of Eq. 1, the horizontal energy axis of a backscattering spectrum can be interpreted as a mass axis, the mass value $M = \infty$ corresponding to the point of incident energy E_0 , with successively lower masses appearing at lower energies.

The spectrum shows three peaks due to the three atomic species and spaced in energy according to the scattering kinetics of Eq. 1. The widths of each of the three profiles, measured at half

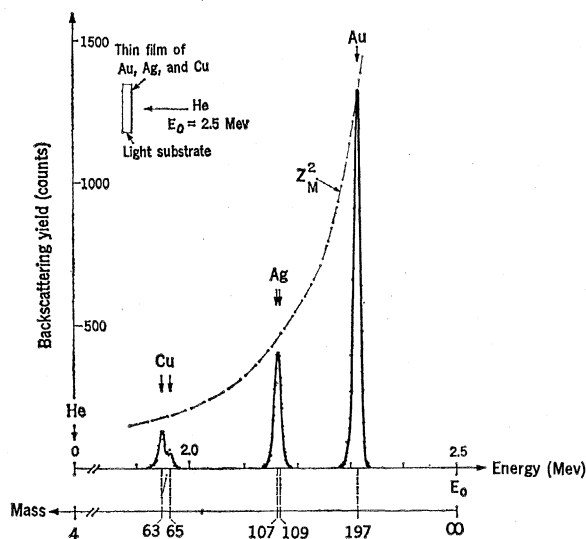


Fig. 2. Backscattering spectrum of a very thin film composed of approximately equal numbers of copper, silver, and gold atoms. Gold (mass number 197) scatters the helium particles more efficiently than silver (mass numbers 107 and 109) or even copper (mass numbers 63 and 65) because the scattering cross section increases as the square of the atomic number Z . (The atomic number is approximately half the mass number.) The width of the gold signal is caused by the finite resolution of the detection system. The backscattering angle is 164° .

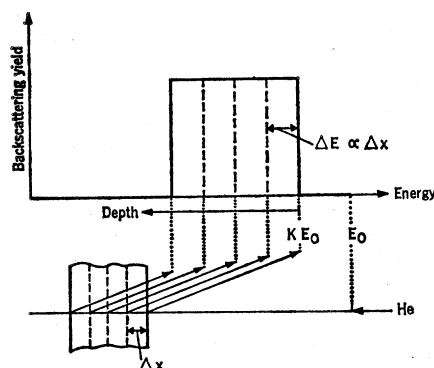


Fig. 3. Depth perception is based on the loss of energy experienced by the incident particle (for example, helium) as it penetrates into the target before the scattering event and as it escapes out of the target again after the scattering event. The energy axis can be converted into a depth scale. The conversion factor depends on the composition of the substrate, the energy of the incident particle, and its mass.

maximum, are different. This difference is due to the fact that there is only one stable isotope of gold (mass number 197) but there are two stable isotopes of silver (mass numbers 107 and 109) and two of copper (mass numbers 63 and 65). Since the energy resolution was modest in this case, the doublet for copper is barely resolved and that for silver appears only as a broadening. With such resolution, two heavy elements can be distinguished only if they differ by at least 10 atomic mass units. It would not be possible to tell apart lead (mass numbers 204 to 208) and mercury (mass numbers 196 to 204), but either could very well be distinguished from tungsten (mass numbers 180 to 186). At the other end of the scale, isotopes can be identified up to about mass 40 (that is, within the first three periods of the periodic table of elements). Although it is possible to improve system resolution, greater energy separation and thus mass discrimination can also be achieved if a higher beam energy E_0 or a heavier analyzing particle is used.

The area under each of the peaks in Fig. 2 is proportional to the number of atoms of each type in the specimen and to the scattering cross section σ of each atom. This cross section varies with beam energy E_0 , the atomic numbers Z_m and Z_M of the projectile and target atoms, respectively, and the scattering angle θ , as expressed approximately by the Rutherford formula

$$\sigma \propto \left(\frac{Z_m Z_M}{E_0} \right)^2 \frac{1}{\sin^4(\theta/2)} \quad (2)$$

Because of the factor Z_M^2 , the sensitivity improves rapidly with the increasing atomic mass of the target. Consequently, the search for small traces of beryllium in organic material may be a losing battle, but the detection of equally small traces of heavy impurities such as mercury, lead, bismuth, and uranium in organic specimens is a much more promising endeavor.

Depth Microscopy

In addition to the mechanism of elastic recoil, which forms the basis for the mass analysis, there is a second mechanism of energy loss in a target. This effect, neglected in the previous description, is responsible for the second major property of the backscattering tool, namely, depth perception.

In short, a finite thickness of the target broadens, toward lower energies, the signal produced by a given element. There is a direct relation between the total thickness of the target and the total width of the signal. The variation of this signal toward decreasing energy reflects the distribution of the element with increasing depth.

Let us consider a thick target as a multiplicity of very thin layers (each Δx thick) as indicated at the bottom of Fig. 3. Each layer will contribute to the flux of backscattered particles. But deeper layers generate signals of slightly lower energies than those of the surface layer, because a certain amount of energy is lost by the analyzing particle on its inward and outward passage through the upper layers (see top of Fig. 3). If the stopping power, that is, the energy lost per amount of mass traversed, is known, the thickness of the target can be determined. One can thus attach yet another scale to the abscissa, starting at the energy point KE_0 , running to the left, and indicating depth or, more accurately, the amount of mass traversed. Values for the energy loss incurred in many materials and at various particle energies can be found in tables of stopping power (13). For depths less than about 1 micron the relation between the thickness of the target and the width of the spectrum is approximately linear; that is, $\Delta E \propto \Delta x$.

If a second element is added to a substrate to form a compound, a second signal will appear in the spectrum at a different energy. Such a case is given in Fig. 4. It shows the backscattering spectrum of a self-supporting

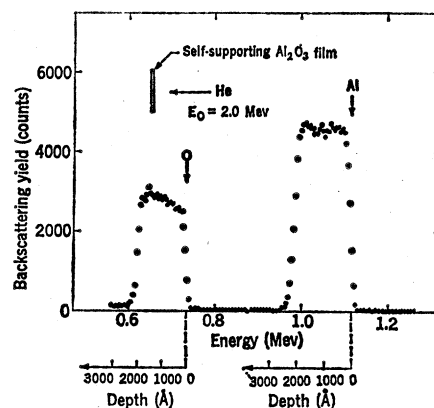


Fig. 4. Backscattering spectrum of a self-supporting aluminum oxide film obtained with 2-million-electron-volt $^4\text{He}^+$ particles at an angle of 164° . Each element in the target generates its own signal with its own individual depth scale. This scale runs to the left with depth zero, the surface, at the position of the upper energy edge of each signal, that is, at KE_0 (see Fig. 3).

film of aluminum oxide (Al_2O_3). Two depth scales are now present, and each, as in the previous case, is proportional to the target thickness. The two scales are slightly different (here by 8 percent), because the stopping power is energy-dependent and the energy of the outgoing particles differs after scattering with either aluminum or oxygen. The two scales also differ from those for the pure elements, because the stopping power depends on the composition of the target. The ratio of the two scales, however, is relatively insensitive to the composition. From such a spectrum, obtained in 15 minutes of exposure, it is possible to establish the thickness of the film, its uniformity in depth, the ratio of aluminum to oxygen, and the nature, amount, and distribution of other impurities, if any.

Energy losses incurred during penetration depend on the mass composition of the target as well as on the mass and energy of the projectile. For helium ions of 1 million electron volts incident on minerals and like substances a typical value of energy loss experienced after both inward and outward traversal is 80 electron volts per angstrom. A detector system with a 16-kiloelectron volt spectral width thus has an effective depth resolution of 200 angstroms. Surface features within a depth of the order of 10^3 angstroms can clearly be resolved. Farther in, the depth resolution deteriorates because the statistical nature of the energy loss produces a spread in the energy of the helium particles. There are few tools whose range of sensitivity falls in this order of magnitude, but there are

many important physical and chemical phenomena which depend critically on the properties of substances at this microscopic level.

Perception of Single-Crystal Structure

In addition to mass identification and depth perception, backscattering possesses yet another property which can be exploited for analytical purposes, namely, its sensitivity to crystalline structure. If the target consists of a single crystal, backscattering yields can be strongly reduced.

The effect is large. One can understand it conceptually by visualizing a single crystal as rows of atoms. When the beam is collinear with the atomic rows, the incident particles can undergo direct impacts almost exclusively with just the first atom of each row; the other atoms are protected from the beam by the surface atoms. The backscattering yield in such an axial orientation of the beam is about two orders of magnitude lower than that observed for a direction for which the beam is not collinear with the atomic rows (random orientation). Simultaneously, in axial orientation, the beam's ability to penetrate the target increases because the trajectories of the penetrating particles are initially parallel to the rows and are confined to the "channels" formed by the atomic rows. This situation is referred to as "channeling." As the particles penetrate deeper into the crystal, they are eventually deflected from the channel ("dechanneled") because of imperfections, thermal vibrations of lattice atoms, and the many small-angle perturbations of the particle trajectory along the channel. As a result, the backscattering yield increases with depth.

If now some atoms in a single crystal are located at positions other than a regular lattice site, they are exposed to the full flux of the channeled incident particles and thus generate additional scattering. By comparing the spectrum of a perfect single crystal in an axial alignment with that of crystals containing appreciable disorder through inclusions or imperfections, one thus obtains information on the amount of that disorder. The effect is large and sensitive, and even minor departures from crystal perfection will be revealed (11).

Figure 5 demonstrates these effects on a gallium arsenide single crystal with various surface preparations. The

backscattering yield for random orientation (curve a) represents a "thick-target" yield, with counts below the high-energy edge of the spectrum representing scattering events below the surface. For example, at 0.4 million electron volts the yield is due to scattering from atoms located about 4000 angstroms below the surface. The yield increases with increasing depth in the sample because the stopping power and the cross section change as the incident particles lose energy when penetrating deeper into the crystal.

When the surface is highly polished by chemical agents, the yield for alignment of the $\langle 110 \rangle$ crystal axis with the incident beam (curve d) is very much smaller than for random orientation. The peak just below the upper edge of the spectrum at about 0.8 million electron volts reveals that some surface disorder still remains. The increase in yield at lower energies is due for the most part to dechanneling. A shorter etch (curve c) produces a less perfect surface, but even a short etch improves the surface condition of a

mechanical polish obtained on a vibratory polisher (curve b). A 1-minute etch reduces the surface peak by about a factor of 8, which indicates a comparable decrease in surface disorder; the yield at lower energies also diminishes because the reduced amount of disorder in the surface layer causes less dechanneling.

In the example shown in Fig. 5, the energy difference of recoils from gallium (mass number 70) and arsenic (mass number 75) was insufficient to resolve the gallium and arsenic signals. At higher beam energies (2.5 million electron volts) two peaks corresponding to scattering from gallium and from arsenic atoms at the surface become clearly visible (14). This mass resolution has been used in conjunction with channeling to study the stoichiometry of the surface region of gallium arsenide as a function surface preparation (15). Such experiments can provide information on problems of crystal structure, radiation damage, polishing, and surface texture. Channeling has also been used extensively in the analysis of ion-implanted semiconductors. The following sections on applications treat examples of backscattering analyses which do not involve the use of channeling.

Dielectric Layers

Backscattering is well suited for monitoring fabrication processes involving thin-film technology such as the growth of oxide layers on metals and semiconductors (16). These processes have great practical significance in the field of metallurgy and electronics. In integrated circuits, for example, dielectric layers of silicon dioxide (SiO_2), silicon nitride (Si_3N_4), or aluminum oxide are frequently used as diffusion masks, protective coatings, and electrically insulating films. These layers are typically 1000 angstroms thick and depend sensitively on growth parameters. For example, backscattering has been applied very successfully to determine the conditions for the stoichiometric growth of silicon nitride (17). In another case involving hydrolytically deposited aluminum oxide, the presence of residual chlorine was identified and correlated with methods of growth (18).

There is at present considerable interest in composite layers of silicon dioxide and silicon nitride on silicon for device applications. The oxide is

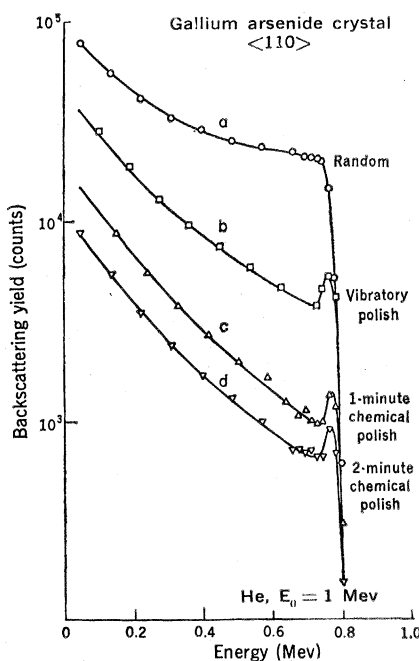


Fig. 5. Backscattering spectrum of a gallium arsenide single crystal. Spectrum a was taken in a "random" orientation of the crystal with respect to the beam. Spectra b-d were taken with the $\langle 110 \rangle$ axis in line with the incident beam. The peaks in spectra b-d are caused by various degrees of imperfection at the crystal surface. Chemical polishing agents produce the least amount of surface damage. A mechanical polish on a vibratory machine causes quite noticeable damage. Note the logarithmic scale for the yield. [Courtesy of J. L. Whitton, Chalk River Nuclear Laboratories]

used to cover the silicon (see insert of Fig. 6A), because it provides the desirable electrical characteristics at this interface, and the silicon nitride protects the oxide layer against contamination by sodium ions. The backscattering spectrum of such a composite structure is shown in Fig. 6A. A schematic representation of this result is also given (Fig. 6B) to indicate the contributions from the various components of the wafer surface. At the position of the silicon edge the spectrum has a step due to the silicon atoms in the nitride layers. There is then a decrease in the height of the spectrum because silicon dioxide contains proportionately less silicon than silicon nitride. Then fol-

lows the increase due to the contribution of the underlying silicon substrate duly shifted to lower energies by the two overlying layers. Since the silicon substrate is thick, this component of the spectrum extends down to the lowest energies. Superposed on this silicon spectrum are two peaks which correspond to helium backscattered from oxygen and nitrogen atoms. The nitrogen signal is at lower energies than the oxygen signal because of the lower mass of the nitrogen atom and this in spite of the fact that the nitride layer lies on top of the oxide layer. Such records reveal the stoichiometry of the layers, their uniformity in depth, and the sharpness of the interfaces.

Metal-Semiconductor Contacts

Backscattering spectrometry has also been used to study the important problem of forming electrical contacts at low temperatures on silicon devices. In integrated circuits, thin metallic layers are vacuum-evaporated and then heated to provide connections between individual circuit elements. Information on these reactions is essentially nonexistent. The depth over which these reactions occur in thin-film metallurgy falls directly in the sensitivity range of the backscattering technique. For example, the fact has long been known and exploited that a thin layer of platinum bonds strongly to silicon after a short

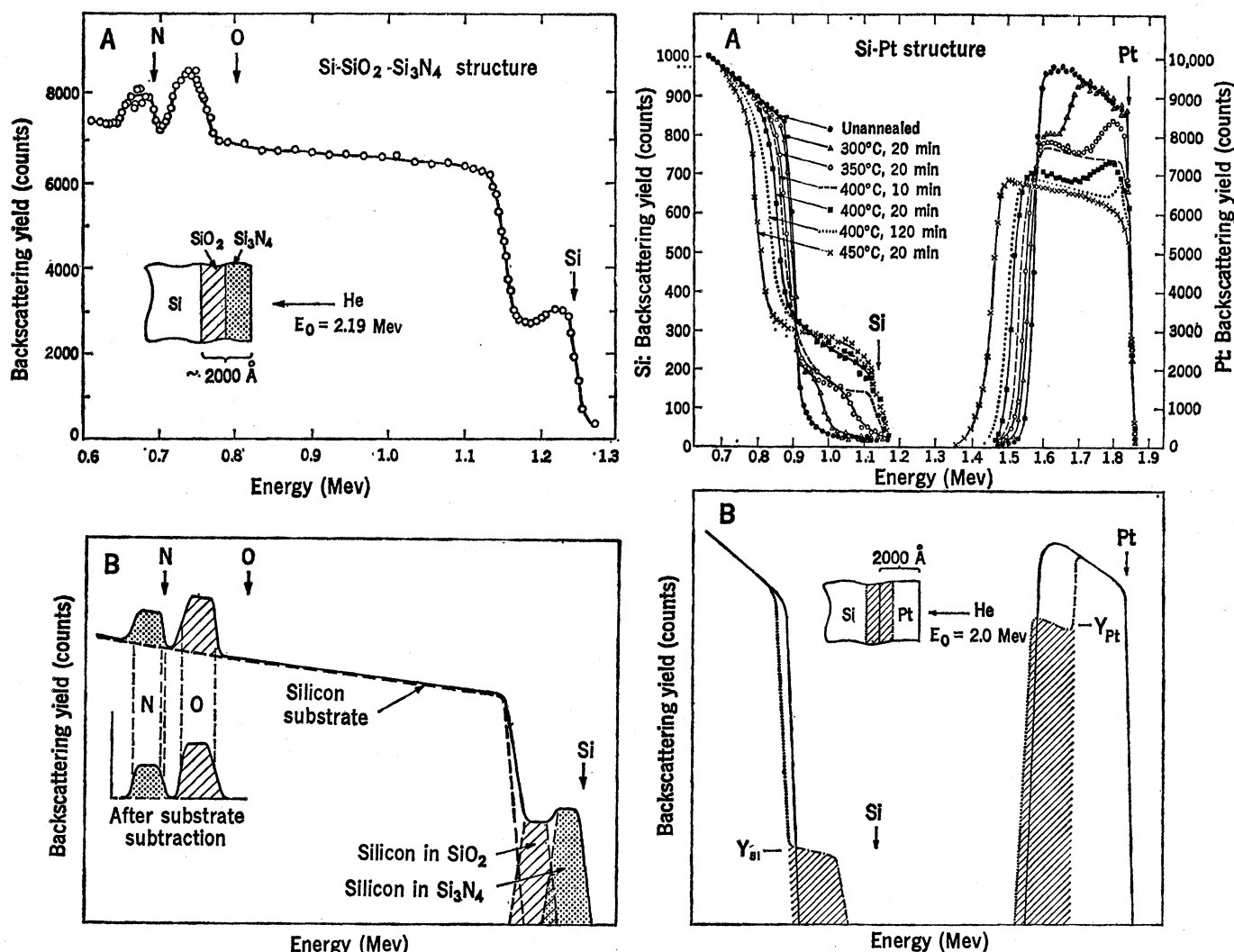


Fig. 6 (left). Composite dielectric layers are used in integrated circuit technology to simultaneously exploit desirable features of silicon oxide and silicon nitride. The thickness and the composition of the two layers can be determined from the backscattering spectrum shown in (A). The schematic below (B) unfolds the spectrum into its components. That the nitride layer lies outermost follows at once from the fact that only the oxygen signal is shifted to lower energies. [Taken from J. Gyulai *et al.* (32)]. [Courtesy of the American Institute of Physics, New York] Fig. 7 (right). (A) Backscattering spectra obtained with 2-million-electron-volt helium from silicon samples covered with a layer of platinum 2000 angstroms thick before and after heat treatment in a nitrogen atmosphere. A PtSi-like compound is formed, first at the interface and then throughout the whole film (300°, 350°, and 400°C curves). Upon further annealing, the layer finally becomes the stable form PtSi (450°C). The composition follows directly from the ratio of the two backscattering yields Y_{Si} and Y_{Pt} (B) and the (known) values of scattering cross sections and stopping power for silicon and platinum. [(A) adapted from (19)]. [Courtesy of the American Institute of Physics, New York]

anneal at temperatures well below the eutectic temperature (980°C). The series of spectra shown in Fig. 7A has revealed what happens (19). Initially, the interface is abrupt, as indicated by the sharp edge of the silicon signal. The presence of the overlying platinum film has displaced this edge toward an energy lower than that of an uncovered sample. After a heat treatment at 300° to 350°C a new phase appears at the interface. This is indicated by the appearance of steps in both the silicon and platinum signals. The ratios of the corresponding backscattering yields of silicon to platinum (shaded portion in the schematic diagram of Fig. 7B)

establish that Pt₂Si-like compounds are formed initially. After a prolonged heat treatment the whole platinum layer is transformed into a compound of uniform average composition. It is found from an analysis of the data that the final layer is PtSi with a thickness twice that of the original platinum film. It is this stable form which is used to make reproducible contacts of predetermined thickness in a number of industrial applications.

Backscattering measurements have shown that the migration of silicon at low temperatures is a widespread phenomenon in thin metal-film systems. The migration has been observed in

films of gold, chromium, palladium, and silver, always at temperatures well below the eutectic points. Investigations are presently being pursued on a variety of metal-metal and metal-semiconductor systems in an effort to characterize these thin-film reactions.

Metals

Iron rusts and metals corrode. It is the stability of the oxide layer which determines how rapidly such processes take place. Properties of magnetic layers also change on oxidation. It is known, for example, that the magnetic

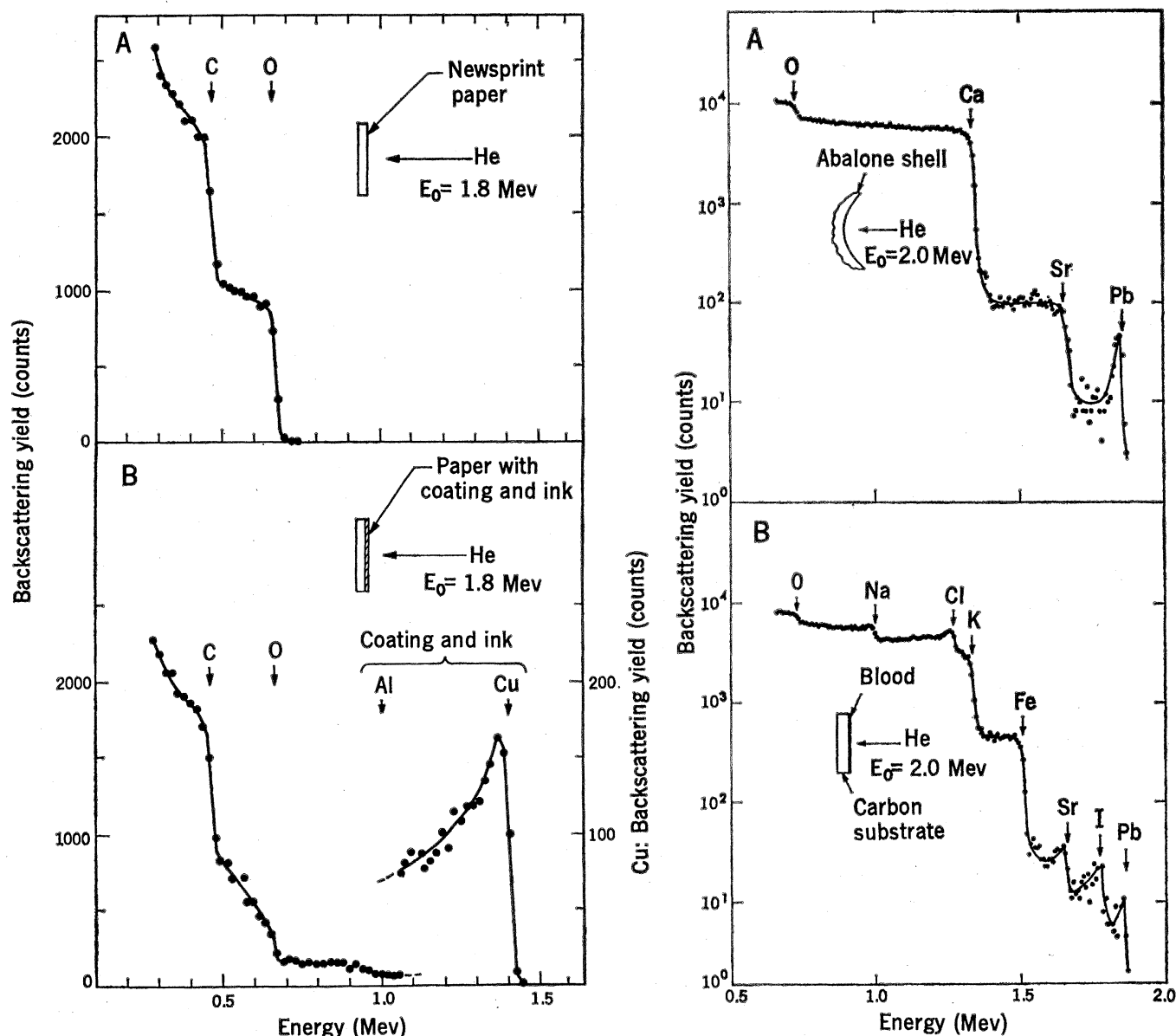


Fig. 8 (left). Backscattering spectra of (A) plain newsprint paper and of (B) coated paper with printing. The presence of copper in the ink and of coating on the paper is clearly visible in (B). The copper signal is enlarged ten times (right-hand scale). [Courtesy of L. Eriksson, Swedish Forest Products Research Laboratory, Stockholm] Fig. 9 (right). (A) The backscattering spectrum of the inner side of an abalone shell; (B) the spectrum of whole human blood obtained by applying only a smear of blood to a clean carbon substrate. The blood was first hemolyzed to break up the blood cells.

moment of Permalloy films (80 percent nickel and 20 percent iron) decreases when an oxide layer is formed by heating. The nature of the layer was unknown until backscattering measurements identified the layer as nickel-free iron oxide. Since the Permalloy composition is initially uniform, a net transport of iron toward the surface must actually take place during oxidation at temperatures not much above 110°C (20).

Another interesting magnetic film is manganese-bismuth. It has a low Curie point which makes it compatible with digital information storage by means of a laser beam. Presently, these films are produced by sequential vacuum evaporation of the two constituents. The magnetic properties are then established by thermal cycling to form a compound. The outcome seems to depend on many parameters in the process of fabrication. In this and similar situations, backscattering analysis holds promise as a diagnostic tool at each manufacturing step.

Examples of other recent applications include the analyses of europium, scandium, or vanadium multilayers on Kovar to determine film thicknesses, layer nonuniformities, and the degree of interfacial penetration (21). Another study of the temper embrittlement of steel containing antimony revealed that antimony segregates at fracture surfaces of brittle steel, but ceases to do so after austenitizing (22). Finally, the extreme sensitivity of backscattering spectrometry to elements with heavy mass has been used in studies of the contamination of surfaces, such as silicon, with traces of gold by etching solutions (23).

Paper

Backscattering techniques are also applicable to organic substrates. The condition which must be satisfied is that the sample maintain its integrity both under the condition of high vacuum in the scattering chamber and under exposure to the analyzing beam. This still allows for a wide variety of materials. Although no detailed investigations have yet been completed, preliminary results are encouraging.

Technical problems of economic importance are the applications of coating to paper and of ink to a coated or uncoated paper. When a thin coating of clay and binding medium is applied

on paper, the binding medium tends to migrate into the paper. This migration can result in poor properties of the paper when it comes to printing. Similar problems of penetration exist with inks. Figure 8 shows two spectra, one (Fig. 8A) from a newsprint paper containing no additives and the other (Fig. 8B) from coated paper to which has been applied a standard blue printing color containing copper (24). The counts above 0.7 million electron volts are the signal from the clay, whereas the peak at the highest energy comes from the copper. Once again, these spectra show the power of backscattering in analyzing problems related to surface composition.

Thick Targets

Thus far, we have considered applications to problems associated with thin films. Many of the same questions can of course be studied also in thick substrates and with little effort required for sample preparation. For example,

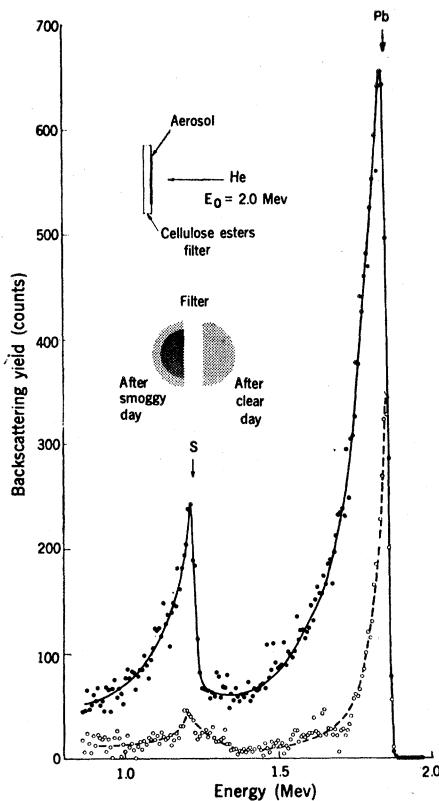


Fig. 10. The spectrum of microparticles collected at night on filters in the Los Angeles basin, between two clear days (dashed line) and after a smoggy day (solid line). The amount of sulfur present varies much, but lead is everpresent. The insert shows half of each filter used in the experiments.

the distribution of impurity or dopant atoms can be followed down to depths of about 1 micron at atomic concentrations of 10^{-5} to 10^{-3} percent, depending on the mass ratio of host to impurity. Measurements of this nature have been carried out for arsenic (an electrically active dopant element) in silicon and for gold in gallium arsenide.

Figure 9A shows the backscattering spectrum of the mother-of-pearl which covers the inside of abalone shells, and Fig. 9B shows the spectrum of a smear of human blood on a carbon substrate. The presence of certain elements in the targets shows up at a glance. Whether the lead content of this abalone shell is abnormal or not remains to be established. In the blood sample, the higher mass impurities tentatively identified as strontium, iodine, and lead all display peaked signals. This indicates that the elements are concentrated near the surface and may actually be contaminants introduced by handling.

Filters containing only carbon, oxygen, and hydrogen form convenient substrates with which to analyze gases and liquids for impurities of medium or heavy mass. Figure 10 shows backscattering spectra of two filters used to monitor air pollution in the Los Angeles basin. Both samples were collected between midnight and 5 a.m., one after a clear day and the other after a smoggy day. The volume of filtered air corresponds to that inhaled by an adult in 1 to 2 days. The change in air pollution shows up plainly in the records; lead and sulfur stand out as major constituents. Such spectra can be obtained typically in 10 minutes, from samples a few square millimeters in area. It is noteworthy that one of the very first applications of backscattering, in 1949, was concerned with the analysis of smog (5).

Sensitivity and Limitations

Backscattering microscopy can be performed over a wide range of beam energies and with many atomic species as projectiles. Only a few combinations have actually been tested so far, but the accumulated experience available suffices to give a rough idea of the performance one can expect in each energy range (see Table 1). We consider here the sensitivity and limitations for helium projectiles. In the region of 1 kiloelectron volt, simple collision kinematics begins to hold and, with

Table 1. Comparison of estimated values for the accessible depth and for the depth resolution obtained at various energies of the incident particle.

Energy range (kev)	Particle	Energy analyzer	Accessible depth (Å)	Depth resolution (Å)	Reference
0.5-2.0	He ⁺ , Ne ⁺	Electrostatic analyzer	Surface	Several angstroms	(29)
20-200	H ⁺ , He ⁺	Electrostatic analyzer	~500	≲ 10	(30)
200-300	H ⁺ , He ²⁺	Surface barrier detector	~1000	≲ 100	(31)
1000-3000	He ⁺	Surface barrier detector	~10,000	≲ 300	(16)

electrostatic (or magnetic) analyzers, mass resolution is already feasible (25). The depth range is essentially nil. The beam penetration increases with increasing energy, and so does the depth accessible to analysis. The fraction of backscattered particles decreases rapidly, however (Eq. 2). With surface barrier detectors, the required times and the doses of exposure can be cut down, but at the cost of poorer resolution. Above about 3 million electron volts nuclear reactions begin to dominate.

The sensitivity also varies with energy. Most applications have so far been in the range from 1 to 3 million electron volts. Figure 11 indicates approximately how well two components of a diatomic substance can be determined by helium backscattering in that energy range. A total number of 10^4 counts per energy channel has been assumed, which is roughly typical for exposure times, doses, and detector

systems currently in use. For example, in silicon nitride, where the two constituents have atomic numbers Z_{heavy} and Z_{light} forming a ratio $Z_{\text{heavy}}/Z_{\text{light}} = 2$, and where the atomic concentrations N_{heavy} and N_{light} of the compound have a ratio $N_{\text{heavy}}/N_{\text{light}} = 3/4$, the relative error $(\Delta N/N)_{\text{light}}$ for the light element nitrogen will be about 5 percent (see dashed lines in Fig. 11). But for arsenic in silicon, where the ratio $Z_{\text{heavy}}/Z_{\text{light}}$ is also about 2, the heavy element arsenic can be measured to the same relative accuracy of 5 percent = $(\Delta N/N)_{\text{heavy}}$ at a concentration ratio $N_{\text{heavy}}/N_{\text{light}}$ of only 10^{-2} . The values actually obtained may depart from those given in Fig. 11 by as much as a factor of 4. This was true, for example, for studies of antimony in silicon ($Z_{\text{heavy}}/Z_{\text{light}} = 3.7$) where a value of $(\Delta N/N)_{\text{heavy}} = 10$ percent was found for a concentration ratio $N_{\text{heavy}}/N_{\text{light}}$ of 4×10^{-5} (14). It is clear, for instance, that quantitative analyses

of trace impurities in relative amounts of 10^{-6} or 10^{-8} are beyond the capability of this technique. However, surface impurities consisting of heavy atoms have been detected at levels of 10^{-2} to 10^{-3} monolayer (that is, one surface impurity atom for every 10^2 or 10^3 surface atoms); for a beam 1 square millimeter in area, this amounts to about 10^{-11} gram of that impurity.

A particular difficulty is that backscattering records are inherently ambiguous. This is so because the horizontal axis of a spectrum is simultaneously a depth scale and a mass scale. Indeed, a light mass located at the surface of the sample generates a signal which cannot be distinguished, a priori, from that of a heavier mass located beneath the surface. Additional information has to be provided to resolve this ambiguity. This difficulty increases with the complexity of the target. Backscattering microscopy is therefore at its best where only a few elements are present and the general physical makeup of the target is known in advance. The problem of deciphering spectra can be alleviated with computerized methods of data processing [see (2), for example].

Particles heavier than helium can be used as a projectile to expand the mass scale. For example, the segregation of antimony at fracture surfaces of brittle steel was investigated with carbon as the analyzing particle (22). By comparison with a helium beam, this doubles the energy separation between the signals for iron and antimony (see Eq. 1). The gain in mass resolution is less than two, however, because the energy resolution of solid-state detectors decreases with the increasing mass of the detected particle (11). Simultaneously, the stopping power increases, which means that the depth range accessible with a given energy decreases and that the radiation-induced damage concentrates over a shorter range. Practical restrictions usually confine the choice of a projectile atom to a few elements only.

With accelerators in the million-electron-volt range the sensitivity to light elements in a heavier substrate can be much enhanced by properly selecting the energy and species of the beam to induce nuclear reactions in the light nucleus and then monitoring a reaction product. Extensive studies of the oxidation of metals and semiconductors have been carried out on this basis at the Ecole Normale

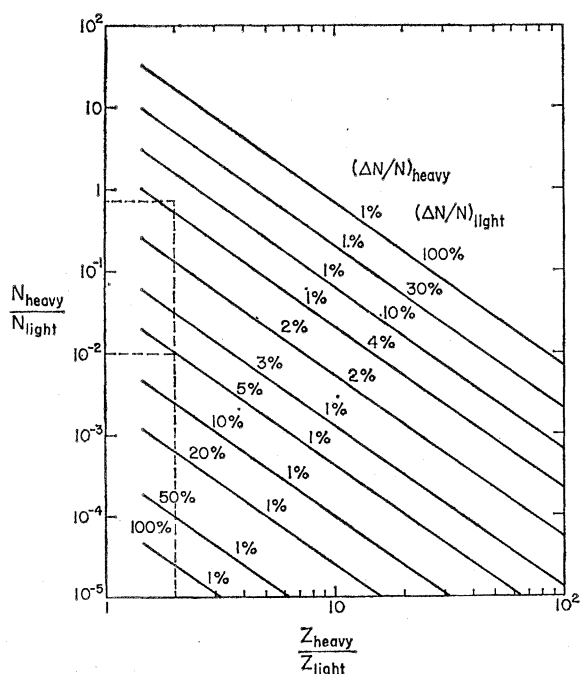


Fig. 11. Estimates of the relative error $\Delta N/N$ with which the atomic concentration N of the heavy and the light atom can be determined by backscattering spectrometry in a two-element system. The variables are the relative composition (ordinate) and the ratio of the atomic number (abscissa) of the two component atoms. These errors were estimated on the assumption that the backscattering signals generated by each element add up to a total yield of 10^4 counts per channel in the final spectrum (minimum statistical error of 1 percent).

Supérieure, in Paris. A review of the subject has been given by Amsel *et al.* (26). X-rays generated by the impinging beam have also been used to identify impurities in a target. Cross sections for the generation of x-rays are high, giving the method high sensitivity (for example, 10^{-11} gram of titanium) (27). In addition, the characteristic energies of x-rays offer the possibility of high specificity. However, depth information is poor.

Damage to the target induced by the beam constitutes a basic limitation of the technique. It is difficult to define this effect quantitatively because different physical properties of the same target may respond with vastly different sensitivities to the same amount of damage. As a rough rule, rigidly bonded inorganic substances tolerate much exposure with little deterioration which, in addition, can often be diminished subsequently by proper annealing. On the other hand, weakly bonded and complex substances such as organic materials can decompose rapidly or even evaporate under the action of the beam in the high vacuum.

Thus far, experiments have been carried out with ion beams typically 1 to 2 square millimeters in area. Since depth resolution is of the order of a few hundred angstroms, or 10^{-4} to 10^{-5} times the linear dimension of the beam spot, the shape of the low-energy side of a thin target spectrum contains precise information about the nonuniformity of the film thickness. A high degree of film uniformity was indicated for examples cited above. Fuller advantage of the depth resolution can be taken by reducing the spot size of the beam. Attempts to improve lateral resolution will continue (28). In the meantime, electron microprobe scans are being used to determine whether target areas of 1 to 2 square millimeters and 1 to 2 square microns give similar results in terms of thickness and composition. Without such precautions, some ambiguity in the interpretation of backscattering spectra remains.

For versatility and flexibility, backscattering systems require high-voltage accelerators as a source for the beam of fast particles. This is no limitation today. A number of accelerators in the million-electron-volt range are used

only part of the time at present, or are totally inactive, both in the United States and elsewhere. This is due in part to the recent cuts in the funding of the basic sciences and also to the obsolescence of small accelerators as research instruments in nuclear physics. One can anticipate a revival of interest in these machines. Their use for backscattering spectrometry also offers good opportunities for fruitful interaction between educational institutions and industry, and so fulfills well the demands of the day for relevancy in research.

Outlook

The most promising feature of backscattering spectrometry is unquestionably its ability to perceive mass distribution over a depth of thousands of angstroms. A large number of physical phenomena depend on the properties of these outermost few thousand angstroms of material. Examples are sliding friction, adhesion, surface hardness, polishing, wetting, alloying, corrosion, electrical conduction through interfaces, and electron-emissive properties. Thin films and thin-film technology constitute another obvious field of application which includes many different subjects ranging from superconductivity, magnetism, electroplating, and anodizing to biocompatible coatings, dry batteries, printing, and others.

Backscattering spectrometry will also find a place among standard methods of microanalysis. The method is at its best when only a limited number of elements are known to be present in a target. It then provides relative compositions with ease. It is thus well adapted to problems in such fields as fractionation, isotope chemistry, and ion implantation, the monitoring and analysis of exhausts, or the testing of industrial products, such as the content of refined ores or the final composition of alloys.

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