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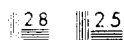
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ION SCATTERING SPECTROMETRY: A VERSATILE TECHNIQUE
FOR A VARIETY OF MATERIALS

William L. Baun
Mechanics and Surface Interactions Branch
Nonmetallic Materials Division

February 1982
Final Report for Period January 1981 - September 1981

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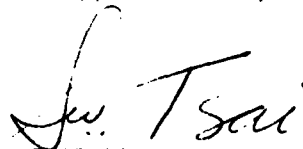
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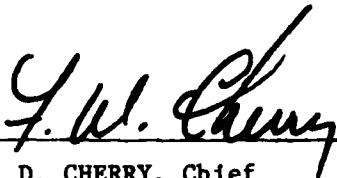


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chemistry and physical and electronic structure of single crystals. The presence of fine features in the spectra enable shadowing and selective neutralization effects to be observed. Striking spectral features are seen in III-V, II-VI, and I-VII compounds. Scattered ion yield curves show a potential for the use of ion scattering spectrometry to determine bonding and electronic structure in some elements. In addition, conventional scattering experiments may be used to determine subtle elemental changes on crystal faces having different orientations. Adsorption-desorption characteristics of different orientations may also be studied in conjunction with the complementary secondary ion mass spectrometry technique.

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FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Non-Metallic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories. The work was initiated under Project 2303, "Surface Phenomena" and WUD #50 "Surface and Interface Properties" monitored by Dr. T. W. Haas.

This report covers work performed in-house during the period January 1981 to September 1981. It represents, in part, an invited presentation at the Surface Analysis Symposium, 181st National American Chemical Society Meeting, held in Atlanta, Georgia, March 29, 1981 to April 3, 1981. It is also to appear shortly as a review article in the journal Surface and Interface Analysis.



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Ion Scattering Spectrometry: A Versatile Technique for a Variety of Materials*

W. I. Baun

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The extraordinary surface sensitivity of low energy ion scattering spectrometry may be applied to the characterization of a wide variety of materials. On the one hand, the surface chemistry may be determined, using ion scattering spectrometry for engineering materials used in diverse technologies such as lubrication and adhesive bonding; such surface chemistry, perhaps involving only a few monolayers, may govern the success or failure of a process. On the other hand, ion scattering spectrometry is also useful in investigating the chemistry and physical and electronic structure of single crystals. The presence of fine features in the spectra enable shadowing and selective neutralization effects to be observed. Striking spectral features are seen in III-V, II-VI, and I-VII compounds. Scattered ion yield curves show a potential for the use of ion scattering spectrometry to determine bonding and electronic structure in some elements. In addition, conventional scattering experiments may be used to determine subtle elemental changes on crystal faces having different orientations. Adsorption-desorption characteristics of different orientations may also be studied in conjunction with the complementary secondary ion mass spectrometry technique.

INTRODUCTION

Low energy ion scattering spectrometry (ISS) using noble gas ions in the energy range 0.1–5 keV has been used for a variety of purposes since the original work of Smith.¹ Applications² and Reviews³ of ISS as a surface analytical tool have appeared and the method is currently one of the major tools for the surface scientist. The chief advantage of ISS lies in its high sensitivity for the first atomic layer, which results from a large scattering cross section and strong neutralization following ion penetration in the solid.

This high probability of interaction with surface atoms also makes the technique ideal for the study of fundamental collision processes of particles with solids. ISS has been used to determine surface structure on single crystals and on adsorbed species.^{4–6} A very recent development is the use of alkali ions which do not suffer from the high probability for neutralization in one collision, and therefore produce scattering spectra dominated by multiple scattering effects.⁷ The comparison of noble and active gas ion scattering at various orientations should prove useful in structure determination.

Observations of structure on scattered ion yield curves^{8,9} indicate that complex electronic ion-atom interactions are occurring. In some cases this structure is oscillatory in nature and is attributed to resonance charge exchange (RCE) processes. Further, it is observed that the yield curve structure for a given element may be different in different compounds, suggesting that chemical information may be gleaned from ion scattering spectra.

* paper presented at the 181st American Chemical Society Meeting, Atlanta, Georgia (1981). Symposium on Use of Surface Science Techniques in Solving Analytical Problems.

Other inelastic interactions between ion and atom are observed in the form of fine structure, straggling, spectral shifts etc. Secondary effects of the ion on the surface such as sputtering, desorption of adsorbed species and emission of photons also occur. In some cases these effects may be used in conjunction with ISS to give elemental chemistry with depth or provide complementary data. All of these phenomena produce a wide variety of information on single or polycrystalline materials. Examples of these varied uses of ion scattering are given in this review.

MECHANICS OF SCATTERING AND EQUIPMENT

The principle of ion scattering is very simple. A monoenergetic beam of low energy ions (usually He⁺, Ne⁺ or Ar⁺) is directed onto a solid surface as shown in Fig. 1.¹⁰ Most of the ions penetrate the solid or are

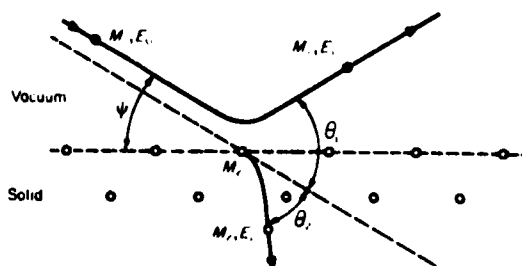


Figure 1. Schematic of the ion scattering process showing a binary collision between an ion of mass M_1 , energy E_0 and a surface atom M_2 at rest before collision; ψ = impact angle, θ = scattering angle (Ref. 10).

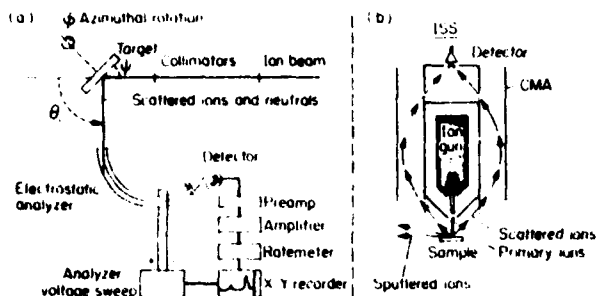


Figure 2. Components for ion scattering spectrometry. (a) system allowing variation in angle of incidence and/or scattering angle and (b) example of commercial system using a cylindrical mirror analyzer (CMA).

reflected as neutral particles. A small number of ions, however, are elastically scattered from the surface atoms. The energy of the backscattered ions may be calculated on the basis of the conservation of energy and momentum, leading to the relationship

$$\frac{E_1}{E_0} = \frac{M_1^2}{(M_1 + M_2)^2} \left[\cos \theta + \left(\frac{M_2^2}{M_1^2} - \sin^2 \theta \right)^{1/2} \right]^2 \quad (1)$$

For 90° scattering, which is often used, the equation reduces to the very simple form

$$\frac{E_1}{E_0} = \frac{M_2 - M_1}{M_1 + M_2} \quad (2)$$

It is this energy ratio E_1/E_0 which is plotted against intensity for the ISS data shown here.

The experimental set-up for low energy ion scattering is shown in Fig. 2. Figure 2(a) shows the arrangement of components which allow the angle of incidence and/or the scattering angle to be changed. This type of instrument would be used for single crystal structure analysis or adsorption-desorption studies. In Fig. 2(b), a fixed angle of incidence and scattering angle are used with a cylindrical mirror analyzer (CMA) and coaxial ion gas. This is the configuration usually used for surface chemical analysis and is typical of commercial instrumentation developed by the 3M Company.¹¹

A positive feature of ion scattering, as compared to most spectroscopies, is the simplicity of the spectra. Binary (elastic) ion scattering results in one peak for each isotope of an element present, occurring at predictable energies as shown in Fig. 3 where calibration curves are shown for the scattering angle resulting from the use of the CMA. Note the steepness of the slope for heavier elements, suggesting the major problem in ISS, limited resolution for some ion-atom interactions. The resolution between elements of similar mass may be improved by going to a heavier ion, for instance from He⁺ to Ne⁺, but even then resolution may be too small to separate the elements. Generally, for best resolution, M_1 should be near the mass of the target element M_2 ($M_1 < M_2$).

The intensity I_A of the ion scattered from the surface atom is given by

$$I_A = I_0 N_A \sigma_A (1 - P_n) \Delta \Omega T \quad (3)$$

where I_0 is the intensity of the primary beam, N_A is the density of the A scattering centers, σ_A is the scattering cross section of A, P_n is the neutralization probability,

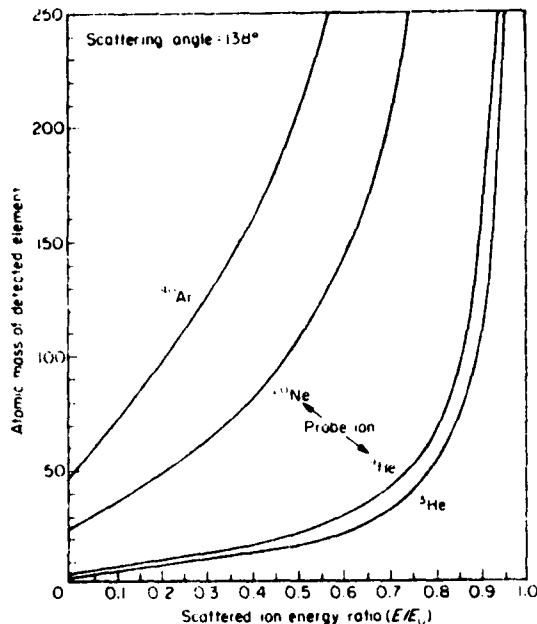


Figure 3. Calibration curves for $^{40}\text{Ar}^+$, $^{20}\text{Ne}^+$, $^4\text{He}^+$ and $^3\text{He}^+$ probe ions, 138° scattering angle.

$\Delta \Omega$ is the angle of analyzer acceptance and T is the analyzer transmission factor. In addition, in many cases, shadowing or shielding must be considered specially when low angles of incidence and/or scattering are used. Scattering cross sections for the ions He⁺ and Ne⁺ for laboratory angles of 90° and 138° have been calculated by Nelson.¹² The spectrometer functions $\Delta \Omega$ and T are constants. The neutralization probability P_n once was considered to be very simple but now is known to be complex, especially for elements exhibiting oscillatory structure on yield curves.^{8,9} Generally, however, despite uncertain geometric and neutralization effects, sensitivity factors for ISS do not vary to the extent of some other techniques such as secondary ion mass spectrometry (SIMS).

USE OF ISS FOR SURFACE CHEMISTRY CHARACTERIZATION

Examples are found in numerous technologies in which performance or failure is governed by chemical differences of one or at most a few monolayers in depth. Microelectronics, lubrication, adhesion, catalysis and many other areas provide such examples. The contamination of surfaces during processing in these and other technologies is often the reason for the failure of final devices. Table 1 shows the many sources of contamination of materials used in adhesive bonding and serves as an example of the importance of slight changes in surface and interface chemistry. Each of the subheadings shown here is a complex system in which chemistry changes can occur, as reported by Solomon and Baun¹³ who outlined possible sources of surface contamination during processing for Al alloy adherends. Following these processing steps, the alloys undergo various chemical etches and mechanical roughening procedures.

Table 1. Sources of contamination in adhesive bonding

1 Raw material (a) Adherend (b) Adhesive	3 Bonding (a) Contamination (b) Diffusion
2 Pre-bonding (a) Chemical (b) Thermal	4 Post-bonding Storage and handling

These treatments alter the chemistry and morphology of the surface as depicted in Fig. 4 where ion scattering spectra are shown for 7050 Al alloy which has been etched with a dilute HF/HNO₃ mixture, leaving F on the surface (Fig. 4a). The alloy is then anodized prior to bonding tests and it is found from the spectrum (Fig. 4b) that the specimen still contains F on the surface, apparently due to aqueous transport phenomena in the electric field. Rather than bonding to a pure Al₂O₃ surface as expected, other ions such as F remain which may affect bondability and, perhaps more importantly, long-term durability.

Following bond testing or failure of a bonded joint during service, analysis by ion scattering proves very useful in determining the exact locus of failure. The surface chemistry information pinpoints the reason for failure and the part of the process which contributes to failure. Failure in a weak boundary layer (WBL) is especially difficult to detect without a very sensitive surface method. Such failure surfaces from a WBL failure were subjected to ISS analysis and the spectra shown in Fig. 5 were obtained from the Ti adherend and commercial adhesive sides of the bond. The data show that a F containing contaminant was inadvertently

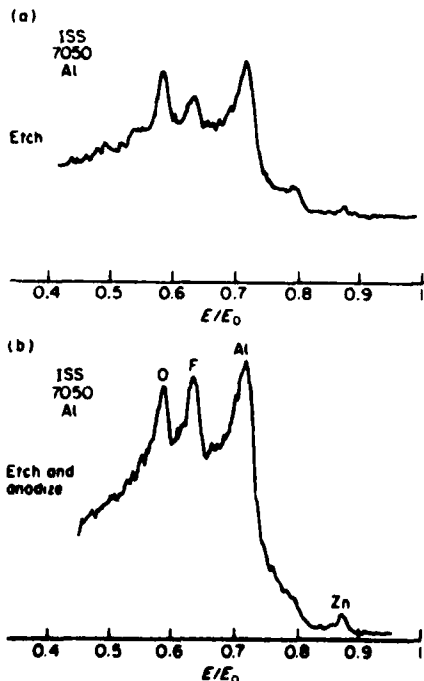


Figure 4. Ion scattering spectra for 7050 aluminum alloy (a) etched in HF/HNO₃ dilute solution; (b) anodized following etching.

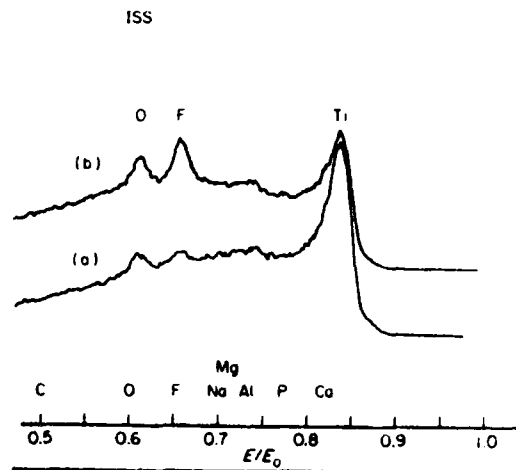


Figure 5. Ion scattering spectra from Ti6Al4V bonded joint failure surfaces (weak boundary layer). (a) adherend; (b) adhesive.

placed in an anodization solution creating a thin F containing layer, along which failure took place. Surfaces such as these may be difficult to analyze by methods using electrons such as Auger electron spectroscopy (AES). In this particular example, the F was desorbed very quickly from the metal surface and its peak did not appear in the AES spectrum. F monitored on a residual gas analyzer (RGA) showed a rapid increase as soon as the electron beam was turned on. The adhesive side did not yield good AES data because of severe charging problems.

Such failure surfaces along a WBL also exist in nature. For instance, in the cleavage of mica it is found by ISS that cleavage has taken place along a layer of K, and that K atoms are equally shared on each cleaved piece and occupy 50% of the surface sites.¹⁴ The ease with which this information is obtained with ISS compared to the difficulty using other methods is very impressive. Twenty or more years of controversy in the literature attest to the problems of unambiguous determination of the mechanism of cleavage in mica and other sheet-like minerals.¹⁵

Still another example where sensitivity only to the surface layer of atoms is found, is in the mechanism of activation of Ba impregnated W dispenser cathodes. Such cathodes are a very bright source of electrons, used for long life and high reliability applications for outer space communication. A proposed life of a dispenser cathode is seen in Fig. 6. During early heating, the Ba compound in the dispenser reacts with W to form metallic Ba which travels along grain boundaries to the surface, lowering the work function and causing electrons to be emitted from the hot surface. As the Ba supply becomes depleted, less Ba covers the surface and emission drops. Certain impurity elements also 'poison' the cathodes and cause reduced electron emission. Analysis of these surfaces with methods such

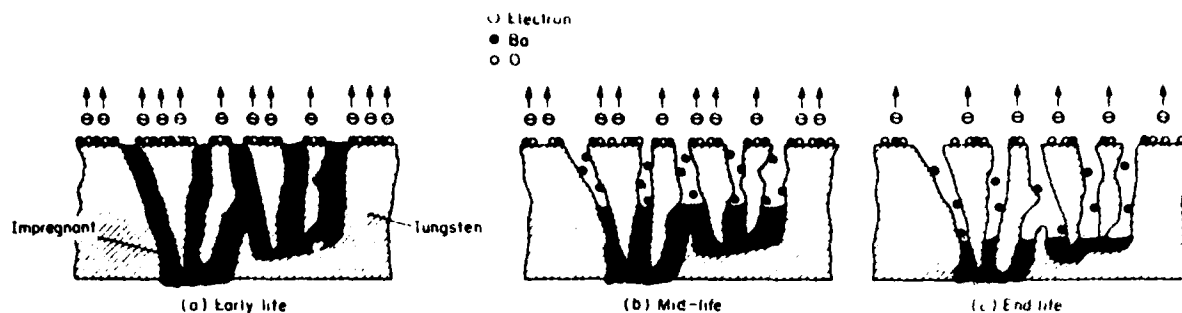


Figure 6. Projected life of a Ba impregnated porous Tungsten cathode (Ref. 40).

as AES and X-ray photoelectron spectroscopy (XPS) do not always give a clear picture of activation and aging mechanisms because atoms deeper than the first layer are involved. In addition, it is possible that the Ba is only adsorbed on the surface and the electron beam in AES causes desorption. Even with ion scattering, initially there was a problem in proving that the W surface was covered with Ba.¹⁶ When typical ion energies were used (1500–2500 V) with a static beam, it appeared that the surface was not totally covered with Ba. When the ion beam was rastered across the surface and beam energies were reduced to 200–300 V, complete coverage of Ba was indicated, but even under these conditions, the Ba was removed very rapidly when the cathode was cooled and Ba ceased to diffuse to the surface.

The area of catalysis is an obvious one in which ISS should be able to contribute to an understanding of the process. The ability to examine the surface of polycrystalline mixed oxide catalysts for the presence and relative abundance of different metallic ions has been an elusive goal for catalyst researchers.¹⁷ Shelef and co-workers¹⁸ showed that on the surface of CuCr_2O_4 the Cr atoms are completely shielded from the surface. Wheeler and Shelef¹⁹ related NO uptake isotherms to chemical composition of aluminate surfaces as determined by ISS. Despite similar chemical formulations of CuAl_2O_4 and CoAl_2O_4 and nearly the same scatter

cross sections of Co and Cu, there appears to be more active scattering by Cu than Co in these spinels. Large differences in NO uptake is seen in Fig. 7, which correlates with the scattering differences for the two spinels. The inference from these studies is that Cu atoms are less apt to be covered by O atoms in the lattice compared to Co and are available for NO adsorption. From this and other work, it appears ISS will be extremely useful in catalysis research.

Other areas investigated by ISS include impurities on ferroelectric crystals,²⁰ mechanisms of diffusion,²¹ diffusion barriers²² and oxidation phenomena in metals and alloys.^{23,24}

Many other illustrations of the use of ISS and comparisons with other techniques could be given, but space is limited. As the technique grows in use, more and more applications will emerge in which ISS is the only technique with sufficient first surface atom sensitivity to provide understanding of a mechanism or process.

USE OF ISS FOR CRYSTALLOGRAPHY

The determination of the position of surface atoms relative to the bulk continues to be a problem. Low energy electron diffraction (LEED) has provided important information for some systems, notably various orientations of Si, but the method is time consuming and for a full dynamic treatment, extremely expensive. Any technique which gives some structural information of surface atoms will serve as a valuable addition to LEED.⁵ The potential of ISS for this purpose was recognized early in the original work by Smith¹ who demonstrated that CO adsorbs on Ni with C bound to the metal and O pointing out from the C.

The first work on single crystal atomic positions was by Strehblow and Smith²⁵ on CdS in which they determined Cd rich and S rich surfaces on the polar crystal. Pioneers in this area include Brongersma *et al.*,²⁶ Heiland and Taglauer,⁵ Englert *et al.*²⁷ and Niehus and Bauer.²⁸

To determine atomic positions, equipment such as that shown in Fig. 2(a) must be used. The crystal is rotated and scattered intensities are noted as incident and/or scattering angles are changed. As different rows of atoms are exposed to the ion beam, certain directions result in more (or less) shadowing or shielding effects, suggesting the atomic arrangement.

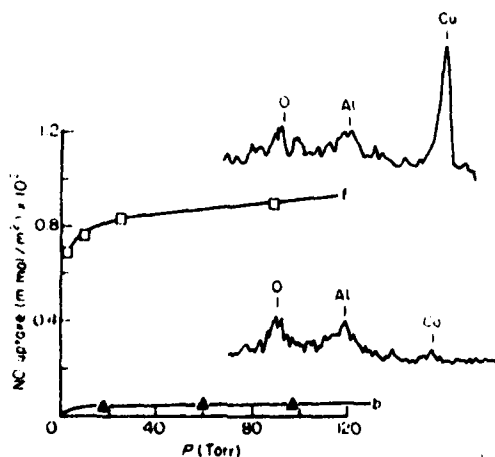


Figure 7. Nitrous oxide uptake and ISS data for CoAl_2O_4 and CuAl_2O_4 (Ref. 19).

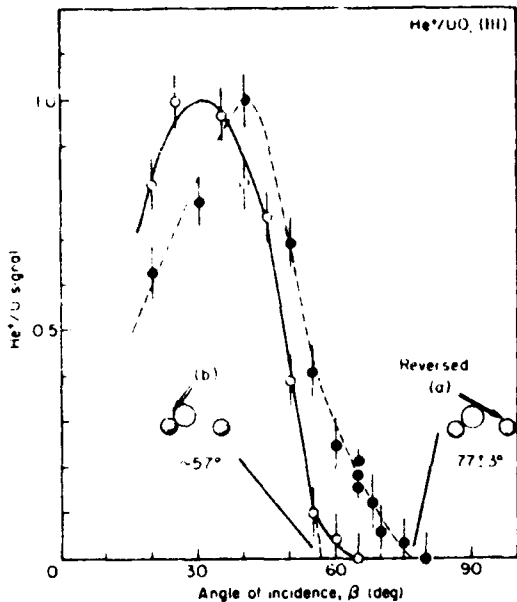


Figure 8. U signal as a function of angle of incidence. Curve (a) is for ions coming from the left and curve (b) is for ions coming from the right (After Ellis and Taylor, Ref. 29).

To illustrate the use of this technique to determine structure, the work of Ellis and Taylor²⁹ in the determination of the O structure on UO_2 (111) will be used. In these studies they have combined LEED with ISS measurements using He^+ at 500 eV. A hard sphere model of the UO (111) planar surface with an outermost O layer is used as a representation of the surface. When the angle of incidence of a probing ion beam is 0° , the postulated outermost layer of O is penetrated and signals corresponding to He scattered from U as well as O should be detected. As the angle of incidence is changed, a critical angle will be reached above which the incident beam will be blocked from reaching the U atoms by the O atoms and only the O peak should be detected. From these authors' data, it is obvious that there will be 2 blocking angles corresponding to beams impinging from the right and the left.

Figure 8 shows results of Ellis and Taylor⁶ for the (111) surface of U. They observe two cutoff angles at $\beta_c = 57^\circ$ and 77° . These cutoff angles are within 3 and 9° respectively of those calculated for a shadow cone model and are considered to be consistent with the center-bonded O model described by these authors.

Very recent work by Taylor and Ellis³⁰ combined LEED with ISS to determine atomic positions on UO_2 (100). They found that a surface periodic distortion or 'zig-zag' existed in the bridge-bonded O array. A model of this UO_2 (100) surface is shown in Fig. 9.

Except for the work at Los Alamos,^{29,30} ISS on single crystals has been done in relatively few laboratories in the USA. McCune has determined the magnitude of the atom shielding effect of O in magnesium silicate³¹ and alkali halide shielding and neutralization phenomena.³² Buck and co-workers at Bell Laboratories have investigated several interesting systems including neon-ion scattering and neutralization on first and second layers of a Ni surface.³³ In this work scattering at different angles and on different orienta-

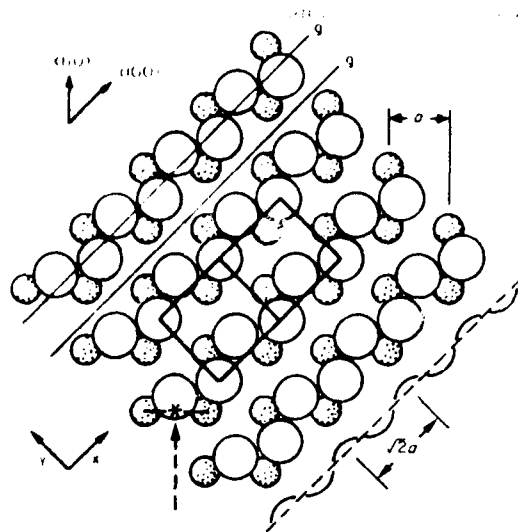


Figure 9. Model of the zig-zag chain O overlayer proposed for UO_2 (100). Small spheres are U atoms. Large spheres are O overlayer atoms. A PLD wave is shown (period = $\sqrt{2}a$) which when coupled with a translation $d_1 = d'$ gives the zig-zag array from the bulk bridge-bond straight chain model. g_1 and g_2 are bulk glide planes (ref. 30).

tions produced significant results in peak shapes and intensities. These authors use a combination time of flight (TOF) and electrostatic analyzer (ESA) to measure scattering of both ions and neutrals. Spectra for two orientations at two angles are shown in Fig. 10. Note the very large differences in scattered intensities as shown in the figure caption. As in the earlier section on chemical analysis, further examples could be given

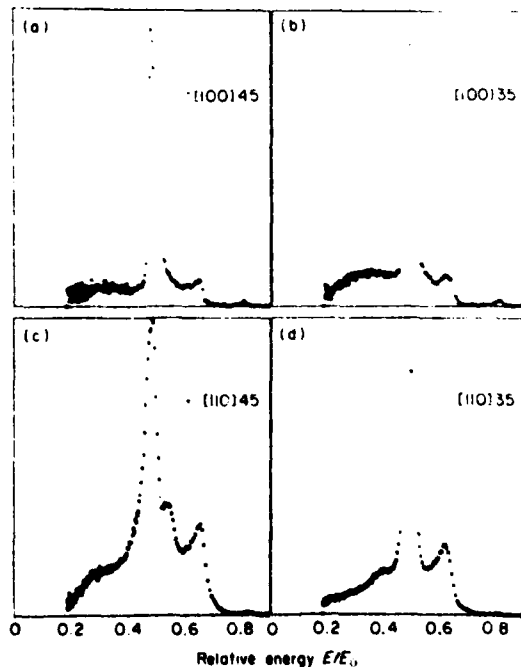


Figure 10. Energy spectra of Ne scattered from Ni. $E_0 = 2.4$ eV, $\theta_L = 90^\circ$. (a) [100]45; (b) [100]35; (c) [110]45; (d) [110]35 ions plus neutrals, derived from TOF spectra. Peak heights are 3400, 3900, 7000 and 18 000 counts respectively (Ref. 33).

for single crystal applications, but space does not permit further treatment.

ISS FOR ELECTRONIC STRUCTURE DETERMINATION

The discovery by Erickson and Smith⁸ (and the expansion of the work by Rusch and Erickson)⁹ that scattered ion yield curves were not always featureless has opened the technique to give possible determination of electronic structure. Various kinds of secondary ion yield curves are observed and have been categorized by Rusch and Erickson⁹ and range from the class I curve as seen in Fig. 11, having no structure, to class II curves in which oscillatory fine structure is observed. It is still not certain what causes all of these effects but in the cases where oscillatory structure is observed, such structure is attributed to RCE between ion and atom. This idea uses a molecular orbital model and says that a quasimolecule is formed very briefly as the ion and atom approach and recede from one another. As the electronic systems of each touch, energy levels of filled and unfilled molecular orbitals may cross and form a new pseudo-molecule. Such nonadiabatic neutralization processes show promise for gaining electronic structure information from the first atom layer of a surface. In the future, it may be discovered that the structure (non-oscillatory) on other yield curves may produce similar information. Categories assigned by Rusch and Erickson⁹ are shown in Table 2³⁴ for various ion-atom pairs.

An example of the use of ion scattering to deduce electronic structure is found in work on HgCdTe epitaxially grown on CdTe and treated and grown in such

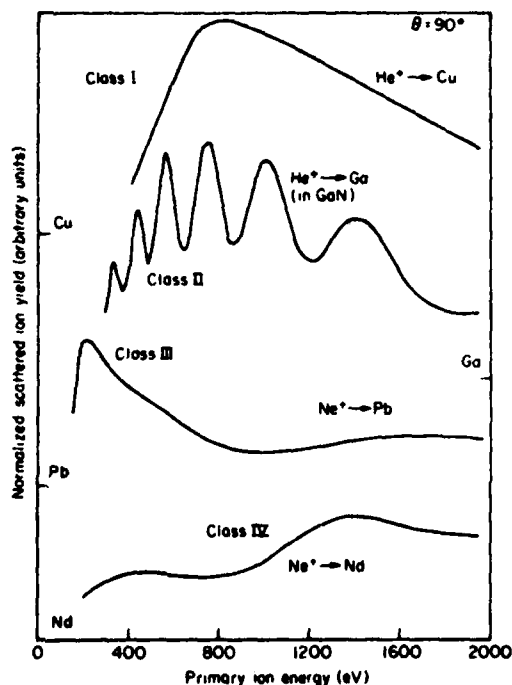


Figure 11. Representative normalized yield curves illustrating the four classes which have been observed for noble gas ion scattering (Ref. 9).

Table 2. Classes of scattered ion yield curves for various ion-atom interactions

Class I	Class II	Class III	Class IV
He ⁺ → Al, Si, Cu, Zn, Zr, Nb, Ag, Cd, Ta, Ti	He ⁺ → Ga, Ge, In, As, Sn, Sb, Pb, Bi	He ⁺ →	He ⁺ → S, Hf, Te, Sa, La, Ce, Nd, Sm, Gd, Dy, Er, Yb
Ne ⁺ → Zn, Sb, Te, W	Ne ⁺ → Ga	Ne ⁺ → Si, S, Ge, Ni, Cu, In, Sn, Sb, Ag, Hf, Pb, Pt, Au	Ne ⁺ → Cd, Ti, La, Ce, Nd, Sm, Gd, Dy, Er, Yb
Ar ⁺ →	Ar ⁺ →	Ar ⁺ → In, Ti, Pb	Ar ⁺ → Cu, Ge, Cd, Sn, Pd, Ag, Sb, Te, La, Ce, Nd, Sm, Gd, Er, Yb, Hf, Pt, Au

a way to achieve (111) faces terminated either by A atoms (Hg, Cd) or by B atoms (Te).³⁵

The scattered ion yield curve for He⁺ scattering from Te (Te metal) and from HgCdTe (111) B are seen in Fig. 12. Here a smooth nearly featureless curve from He scattering from Te is observed as previously reported by Rusch and Erickson.⁹ When He⁺ is scattered from HgCdTe, however, the scattered ion yield curve from Te changes dramatically with increasing energy. The fine structure becomes oscillatory and it appears likely that there is an interaction between the He 1s electrons and Te 4d electrons. This interaction of the He ion with the Te atom may arise due to the changing of bonding and the formation of a molecular orbital in the A^{II}B^{VI} semiconductor compounds. Since each Group II atom is tetrahedrally surrounded by Group VI atoms and vice versa, it is reasonable to assume that each atom has four valence electrons. This suggests that the bonding has a covalent character and that the semiconductor properties of these compounds would be similar to those in the corresponding Group IV elements. The data for the unit cell edge, interatomic separation and energy

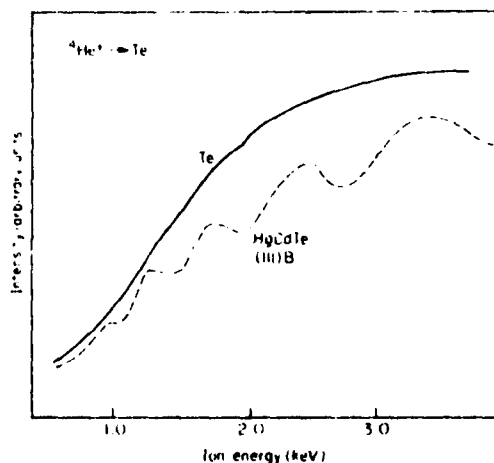


Figure 12. Scattered ion yield curves for He⁺ on Te from elemental Te and from HgCdTe (111) B (Ref. 35).

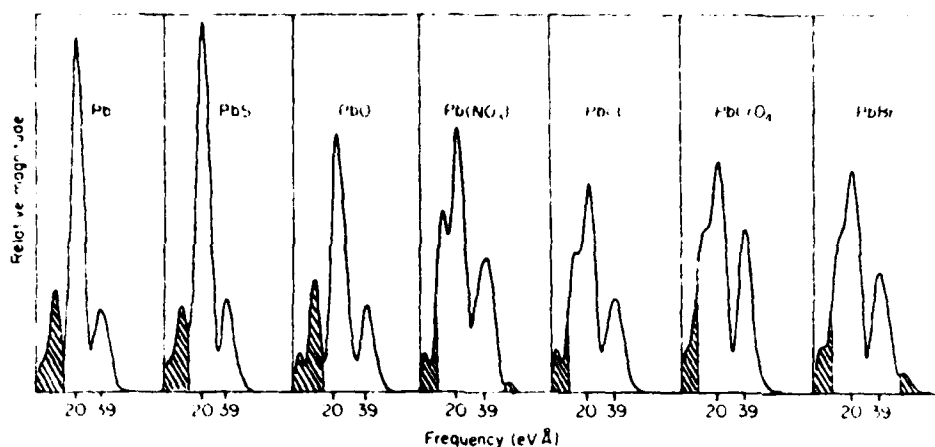


Figure 13. Low frequency portions of the magnitude spectral density functions of lead compounds. Shaded portions should be disregarded. All amplitudes were normalized with respect to PbS (Ref. 37).

gap, shows that Sn very nearly approximates the values for CdTe. The oscillatory fine structure, as observed from He⁺ scattering from Te in HgCdTe, is very similar to Sn⁰ and is attributed to quasisonant charge transfer between He 1s states and the outer d states of these atoms. Christensen *et al.*³⁶ found that the oscillatory structure on He⁺ → Pb resembled the structure seen on He⁺ → Bi when Pb was bonded to an electronegative species such as Cl or Br. This behavior appears to be similar to the results observed here.

In the elemental form the energy of the N_{IV} level of Te (39.8 eV) would not provide an energy match between K electrons in He (24.6 eV). Perhaps the formation of molecular orbitals in d states in HgCdTe provide a match between He⁺ and Te to allow charge transfer.

The recent thesis by Christensen³⁷ details results of many experiments on a number of elements and compounds showing yield curve structure. Christensen found large changes in structure due to chemical bonding. He also developed methods of processing the yield curves to facilitate the comparison of shape and intensity of spectral features. Christensen found that some elements exhibited only one major feature in the magnitude spectral density functions while other elements showed two or more. An example of the final processed curves for some Pb compounds is shown in Fig. 13. Here the change in intensity of the various components is obvious. Using similar curves for Pb-Bi alloys, Christensen was able to plot the intensity of certain

components and achieve a linear relationship with composition.

The use of fine features in the ion scattering spectrum and, in particular, yield curve structure will grow as the understanding of these features increases.

ISS FOR QUANTITATIVE ANALYSIS

Since Haeussler³⁸ recently reviewed quantitative aspects of ISS in this journal, it is not felt necessary to treat the subject. In addition there is not much coverage in the literature concerning quantitative analysis by ISS. Even though scattering cross sections have been calculated,¹² uncertain neutralization (as typified by effects such as oscillatory yield curve structure) make absolute quantitative analysis difficult without standards. Empirical calibrations using pure elements and alloys have been found to be very useful, although surface enrichment in alloys, preferential sputtering and surface roughness all cause difficulties.^{18, 19}

SUMMARY

Low energy ion scattering is a valuable characterization method having the potential to determine chemistry, crystallography and electronic structure of the first layer of atoms on a solid surface.

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