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Ion scattering spectral features in oxides caused by inelastic energy losses

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Shifts of ion-scattering peaks from oxides indicate that the primary beam loses more energy than predicted by the scattering equation. The origin of these shifts is not clear but may be explained by inelastic-collision exchange processes between the noble-gas ion and oxygen on or near the surface. The phenomenon appears to be sensitive to matching energy levels and orbital symmetry of the ions with surface atoms. Other spectral features indicate that the ions penetrate the surface and lose energy in inelastic events beneath the surface. Large changes in relative scattering of the anion and cation in oxides may be caused by either geometric structural effects or selective sputtering phenomena.

Low-energy (~0.1 to 5 keV) ion-scattering spectrometry (ISS) is being used increasingly to determine chemical species at the surface of solids.[1-3] This technique involves bombarding a solid in vacuum with noble-gas ions, dispersing the scattered ions with a suitable spectrometer, and measuring the loss of energy with respect to the original energy of the ion. Noble-gas ions give sharply defined spectra since they lose most energy through a single binary collision with a surface atom. Normally a simple two-body collision model is sufficient to describe the interaction of an ion with a solid target.[4] However, experiments to be described here show that in certain cases, simple ion-scattering theory is not sufficient to explain some spectral effects. In this paper, results are shown partially clarifying previously unexplained anomalies which occur due to inelastic collision energy-loss processes.

Numerous workers have shown the validity of binary ion scattering over a wide energy range of several hundred to several thousand volts on pure materials such as copper[5] and nickel.[6] However, in actual practice peaks are frequently shifted from the theoretical position toward either higher or lower energy. Usually a shift to higher E/E_0 is indicative of specimen charging caused by positive-ion bombardment and emission of Auger electrons resulting in a net positive charge on the sample (especially common for dielectrics). This charge may be neutralized by flooding the sample with low-energy electrons which cause the scattered peaks to return to their correct positions. Shifts to lower E/E_0 have also been reported. Heiland and Taglauer[7] show helium ions scattered by oxygen to shift to lower E/E_0 with decreasing ion-beam energy. Wheeler[8] reported her work on He^+ scattering at 90° from the incoming beam on Ta_2O_5 with silver as a standard. Incredibly (at the time), the "Ta" peak (He^+ scattered by Ta) shifted with decreasing ion-beam energy until it crossed the "Ag" peak to lie on the low-energy side rather than on the high-energy side as it had at high bombardment voltages (>1000 eV).

The binary equation for 90° scattering reduces to the simple

$$\frac{E}{E_0} = \frac{M_{\text{atom}} - M_{\text{ion}}}{M_{\text{atom}} + M_{\text{ion}}} ,$$

where M_{ion} is the mass of the bombarding ion, M_{atom} the mass of the target atom, E_0 the kinetic energy of M_{ion} before the collision, and E the energy of M_{ion} after the collision.

Wheeler's result therefore indicated that $^4He^+$ scattered at low energies from Ta just as though Ta had a smaller mass than Ag. At the time no explanation could be advanced for this peculiar phenomenon.

Wheeler's results were reproduced in the present work. Helium ions were scattered from anodized films on pure Ta using a commercial[9] ISS unit with ion-beam energies of 250 to 2500 V. It was found that both peaks in the spectrum shifted to lower energies as seen from the two spectra plotted in Fig. 1. Besides the unusual shift phenomenon, there is a startling change in relative intensities of He scattered from O and Ta. This voltage dependence of scattered-ion intensities is seen in many oxides and will be discussed later.

There were many possibilities for the cause of the shifts, only two of which were reasonable: Experiments using high and low ion-beam fluxes and a flood of electrons eliminated specimen charging. No possibility for a change in either M_{ion} or M_{atom} was considered. The two remaining possibilities, the ion beam losing energy by another process, and scattering taking place at a scattering angle different from 90°, were considered. Although the latter possibility cannot be completely ruled out, experiments with mixed ion beams, in which only one shifted in scattering energy with voltage and other targets such as Ag (plotted in Fig. 2) and Au, make

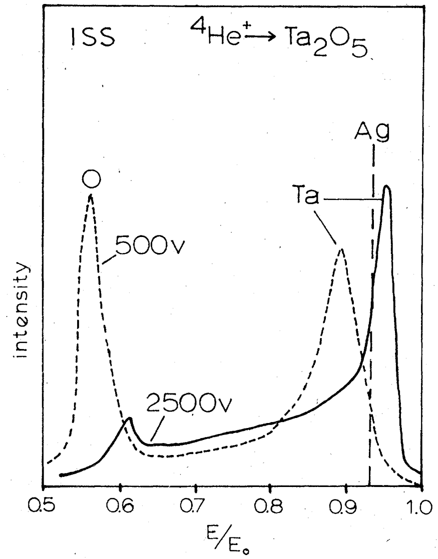

FIG. 1. Ion-scattering spectra from anodized tantalum at 500 and 2500 eV primary ion energy using $^4He^+$. The position of $^4He^+ \to Ag$ is shown for reference (90° scattering).

this alternative very unlikely in the absence of charging. These experiments pointed to an ion-beam energy loss as the source of this shifting. The binary-scattering peak could be returned to the theoretical position at each ion-beam voltage by the addition of approximately 25 V to the ion-beam voltage. Therefore, the shift from the theoretical position ranges from 1% at 2500 V to 10% at 250 V. Because of the large slope of the scattering curves for light ions on heavy atoms, the shift for $He^+ \to Ta$ represents a change in Z of about 40 as shown in Fig. 3. The other peak, $He^+ \to O$ lies on the scattering curve in an area where the slope is much smaller and therefore appears to shift only about

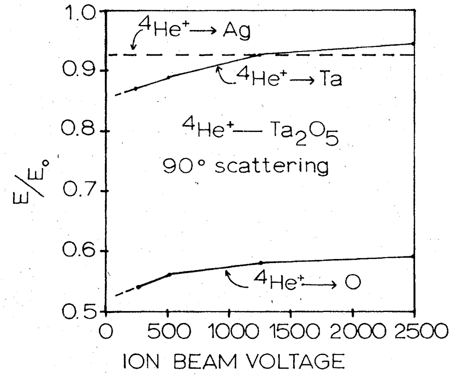

FIG. 2. Plot of E/E_0 vs primary ion-beam energy for $^4He^+ \to Ta_2O_5$ showing linear change in energy of both $^4He^+ \to Ta$ and $^4He^+ \to O$ (90° scattering).

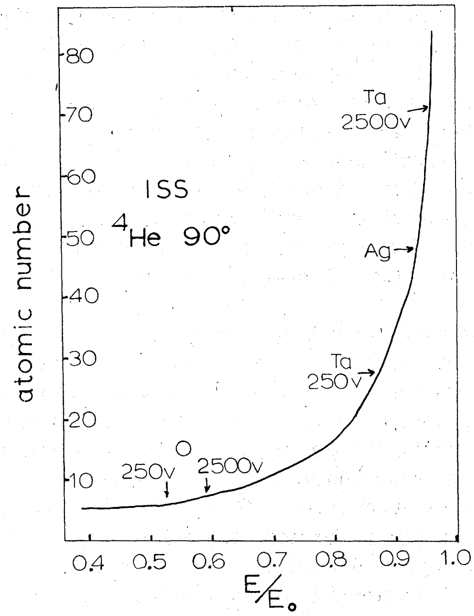

FIG. 3. Scattered-ion fractional energy E/E_0 for ^4He vs atomic number of target. Shifts of Ta- and O-scattered peaks from 2500 to 250 eV are marked on the curve.

one atomic number over the range 250–2500 V, even though the relative shift is the same as for $He^+ \to Ta$.

The scattering experiment was repeated, substituting $^{20}Ne^+$ for $^4He^+$ as the impinging ion. No shift in the $^{20}Ne^+ \to Ta$ scattering peak was observed. Scattering of Ne^+ from oxygen cannot be observed. It is assumed that because energy levels of Ne ($2s = 45$ eV, $2p = 18.3$ eV) (Ref. 10) do not match O levels, there is no exchange. On the other hand, when the experiment was repeated with $^{40}Ar^+$, a shift in the scattered peak with ion-beam potential similar to that shown by He^+ was observed. The Ar $3s$ electron at 25.3 eV (Ref. 10) also matches O in both energy and symmetry. Since it could be considered possible that the Ta $4f$ level 25.0 eV (Ref. 10) may also enter into the reaction, the experiments were repeated using other oxide targets such as WO_3, Nb_2O_5, TiO_2, and ZrO_2. The constant energy loss was observed from these oxides suggesting that the energy loss is associated with the impinging ion and oxygen.

A possible mechanism for this shift is orbital exchange between the helium ion and atoms on the surface (or near the surface, perhaps having already left the surface by a sputtering process). It is well known that a beam of low-energy ions incident on a surface can be neutralized by numerous processes including resonance neutralization followed by secondary electron emission due to Auger deexcitation of the excited atom. It has been found recently that oscillatory cross sections in low-energy ion-scattering yield curves are due to resonant electron exchange processes.[11] Rusch and Erickson[12] have separated these yield curves into four different classes which are correlated with matching of target-atom electronic states with ion-binding energies and with ion-solid orbital symmetries. These results are illustrative of the many ion-solid and ion-gas reactions which can occur.

In the case in point of helium atoms scattering from tantalum oxide, it may be that exchange takes place between He^+ and O in an inelastic collision on or near the surface. This collision may occur either before or after the helium ion backscatters from the heavy tantalum atoms. The molecular-orbital model reviewed by Garcia *et al.*[13] says that a quasimolecule is formed very briefly as the ion and atom approach and recede from each other. As the electronic systems of the two members touch, energy levels of filled and unfilled orbitals may cross, leaving orbitals different from those in which they entered, thus creating vacancies. Subsequent filling of these vacancies may of course produce photons such as visible light[14] and x rays.[15] Radiationless deexcitation mechanisms produce sharp Auger electrons which have been measured for several elements.[16] Photon emission (as well as secondary ion emission) is greatly enhanced by the presence of oxygen[17] on the surface. It is suggested that all of these occurrences, including the one presently described, and the role oxygen plays in these processes, are closely related. The description of each of these phenomena will hopefully allow a full explanation of the complex mechanism of the interaction of ions with solid surfaces.

One problem exists in the explanation of exchange between He^+ and O which results in a constant energy loss. The large variation in ion energy would change the distance of closest approach of the ion and atom and would not appear to result in a constant energy defect. However, perhaps there is a threshold effect which occurs when an ion is just energetic enough to reach the distance where orbital-level crossing occurs. Also, it may be possible that the heavy element Ta, or the lattice arrangement, in some way forces a constant distance of closest approach.

In addition to the constant peak energy loss at each bombarding voltage, ion-scattering curves from oxidized tantalum also exhibit features due to inelastic losses from collisions beneath the surface. The high background between the oxygen and tantalum scattered peaks as seen in the 90° spectra in Fig. 1 results from ions penetrating the surface and losing various amounts of energy before leaving the solid. Perhaps, as mentioned earlier, since there is such a great probability for neutralization in just one collision, these losses occur to the neutral species which then reionize at the last hard collision before entering the vacuum phase.

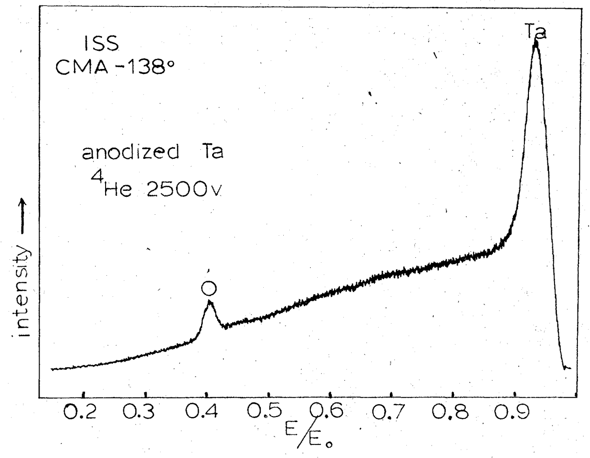

FIG. 4. Ion-scattering spectrum from anodized tantalum at 2500 eV primary ion energy using $^4He^+$ (138° scattering).

These inelastic losses increase with increasing ion-beam energy as shown by Sharma and Buck.[18] The inelastic features are affected by geometry and are accentuated at larger incident and scattering angles as seen in Fig. 4 where the ^4He scattering curve from anodized tantalum is shown. Apparently at larger angles the ions are able to penetrate deeper and scatter from greater depths than when they enter and leave at lower angles. Not only are light ion beams so affected, but also heavier ions such as Ne^+ and Ar^+. Sharma and Buck[18] show scattering spectra from Ne^+, Ar^+, and Kr^+ at voltages up to 30 kV in which the low-energy structure is very intense. The presence of oxygen and other contaminants on the surface influences the structure due to inelastic effects even in heavy ions in which under normal conditions no binary scattering can be observed ($M_{ion} > M_{atom}$). An example of this effect is seen in Fig. 5 where Ne^+ scattering from tantalum is plotted. The solid curve (1) represents scattering from a natural oxide on pure tantalum. Sputtering was continued for 1 h during which the scattering curve changed smoothly to curve 2 which represents scattering from a clean Ta surface. Ball and co-workers[19] showed He^+ scattering curves from a dirty Ta Al alloy in which very little binary scattering was in evidence, with the scattering maximum located in a broad band to lower energies from the theoretical binary-scattering position. Prigge *et al.*[20] showed similar low-energy broadening and peak shifts in a study of oxygen single-crystal tungsten, which they ascribed

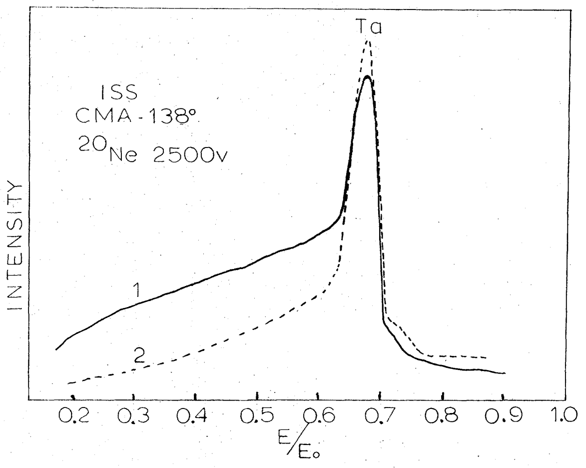

FIG. 5. Ion-scattering spectra from tantalum metal using ^{20}Ne at 2500 eV, Curve 1 (solid) is first spectrum on contaminated surface. Curve 2 (dashed) is after one hour of sputtering to obtain clean surface.

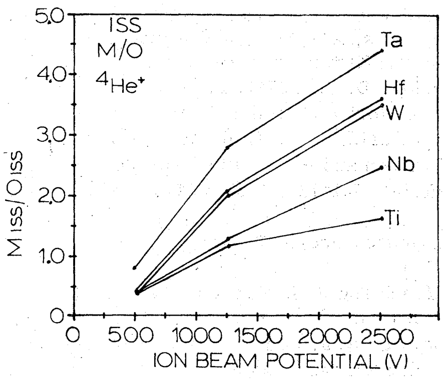

FIG. 6. Ratio on the scattered intensity from the metal (M_{ISS}) to the oxygen (O_{ISS}) for ^{4}He scattering plotted vs ion-beam potential.

to double scattering, first from oxygen and then from tungsten. They found that the best sensitivity for oxygen was obtained at low ion energies because the penetration and inelastic effects were minimized and most scattering took place in the first layer (occupied by oxygen atoms).

Similar geometrical effects were seen in this work on anodized films on polycrystalline materials. At the highest ion energy used here (2500 V) He$^+$ scattering from the metal in the anodized oxide was very strong and scattering from oxygen correspondingly weak. As the ion accelerating potential is decreased, the oxygen becomes more prominent at the expense of the metal ion. The same trend was observed in each of the oxides as seen in Fig. 6 where the ratio of the intensity of the scattered peak from the metal to the intensity of the oxygen peak is plotted against ion-beam voltage for several oxides. Note the striking effect of the mass of the metal on the intensities of the scattered peaks. These results could be interpreted on the basis of geometrical effects as in the referenced work on tungsten[20] or could be ascribed to greatly enhanced oxygen sputtering due to backscattering at higher voltages. It has been demonstrated that backscattered ions make a large contribution to the sputtering yield for the irradiation of a heavy target with a light ion.[21] For copper on tantalum it was estimated that possibly 50% of the Cu sputtering events result from backscattering.[21] Presumably the effect would be even more striking for oxygen on tantalum. The sputtering explanation requires that at high ion-beam energies the oxygen atoms are removed more rapidly than they diffuse to the surface to replenish the atoms lost. At lower ion-beam energies the ions would not have sufficient energy to penetrate into the surface and the backscattered enhancement of the oxygen sputtering would be minimized. Binary scattering could then take place primarily at the surface between the ion and oxygen, with low probability for scattering between the ion and the metal atom because of shadowing effects.

The present experimental results indicate that several inelastic collision phenomena take place between noble-gas ions and oxide surfaces which can be studied by ion-scattering spectrometry. Perhaps these data coupled with the results of experiments on photon, electron, and ion emission from ion-bombarded solids, will help form a clearer picture of the ion-atom interactions which take place.

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