APPLICATION NOTE

Ion Scattering Spectroscopy

Ion Scattering Spectroscopy (ISS), also known as - low energy ion scattering (LEIS), is a technique in which a beam of ions is scattered by a surface. The kinetic energy of scattered ions is measured; peaks are observed corresponding to elastic scattering of ions from atoms at the surface of the sample. Each element at the sample surface produces a peak at a different measured kinetic energy due to momentum transfer between the incident ion and atom. The scattered ion and the scattering atom are normally of different masses, but the total momentum of the atom and ion is conserved. Therefore, as the initially "stationary" atom recoils, some kinetic energy is lost from the scattered ion. The quantity of energy lost from the ion depends on the relative masses of the atom and ion.

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An ion scattering spectrum will typically contain one peak for each element present, with their separation in energy relating to the relative atomic masses of those elements. In some cases, different isotopes of the same element can be resolved, although this usually requires a heavier primary ion than He⁺. Strong scattering signals are limited essentially to the topmost layer of atoms, so ISS is extremely surface-sensitive. This means that for best results the sample must be very clean, as even a small quantity of surface contaminant can strongly influence the ion scattering spectrum. Figure 1 shows the experimental geometry.
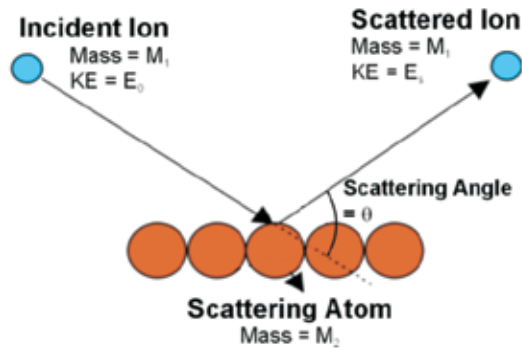

Figure 1: Experimental geometry for ISS experiments

The absolute kinetic energy (E_s) of each peak also depends on the energy of the scattered ion beam (E_0) because ISS is an energy loss technique. The relevant quantity when dealing with ISS is the ratio of the scattered and incident ion energies, E/E_0.

The angle through which the ions are scattered (θ) is also important. Where the ion source and detector are fixed, the angle is simply one parameter that must be included in the calculations.

Calculations

Equation 1 shows how the energy of a scattered ion peak is related to the other relevant factors:
Where:

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

E_S = Kinetic Energy of Scattered Ion

M_1 = Relative Atomic Mass of Scattered Ion

E_0 = Kinetic Energy of Primary Ion Beam

M_2 = Relative Atomic Mass of Scattering Surface Atom

θ = Scattering Angle

For a given instrument, θ is normally a constant. M_1 is constant for a given source gas (usually He, but sometimes Ne, Ar and other inert gases are used), and E_0 is normally constant in a given experiment. So, in principle, Equation 1 can be used to determine the mass of a scattering atom, M_2, from its peak position in the spectrum, or to predict the position of a peak for a given atom.

E_0 is not always known with sufficient accuracy at the start of an experiment. The solution to this is to calibrate the energy using a standard sample, preferably of a pure, metallic element such as gold, for which M_2 is known. Once the scattered peak energy from the standard sample is measured, the only remaining unknown is E_0, which can be calculated using Equation 1.

Once E_0 is known, the main aim of ISS is usually to associate scattered peaks of energy E_S with atoms of mass M_2. Equation 1 may be simplified to a quadratic equation in (M_2/M_1).

Let $M = (M_2/M_1)$, $E = (E_S/E_0)$, $C = \cos\theta$, $S = \sin\theta$, which lets us rewrite Equation 1 as:

$$E = \left[\frac{C + \left[M^2 - S^2 \right]^{0.5}}{1 + M} \right]$$

This can be rearranged to produce equation 2. This equation may be used to determine the mass of a scattering atom from the kinetic energy of its ISS peak, once the primary beam energy has been calculated.

$$M = \frac{(2CE^{0.5} - 2E) + [(2CE^{0.5} - 2E)^2 - 4(1 - E)(-[E^{0.5} - C]^2 - S^2)]^{0.5}}{2(1-E))}$$

or

$$M = \frac{M_1(2CE^{0.5} - 2E) + [(2CE^{0.5} - 2E)^2 - 4(1-E)(-[E^{0.5} \; C]^2 \; S^2)]^{0.5}}{2(1-E))}$$

(2)

Examples

Consider at first the case where the primary ion energy is not known. He⁺ ions of ~1 keV energy are scattered from a gold substrate, using a Thermo Scientific™ ESCALAB™ Xi⁺ XPS Microprobe. A strong peak attributable to scattering from Au is observed at 877 eV kinetic energy. So, $M_1 = 4$, $M_2 = 197$, $\theta = 130°$, $E_S = 877$.

The primary beam energy E_0 is calculated using the first part of Equation 1, rearranging to:

$$E_0 = \frac{E}{\left[\frac{\cos\theta \left[\left(\frac{M_2}{M_1} \right)^2 - \sin^2\theta \right]^{0.5}}{1 + \frac{M_2}{M_1}} \right]^2}$$

$$= \frac{877}{\left[\frac{\cos 130 \left[\left(\frac{197}{4} \right)^2 - \sin^2 130 \right]^{0.5}}{1 + \frac{197}{4}} \right]^2}$$

$= 937$

Thus, the primary beam energy is determined to be 937 eV. From this we can determine the masses of peaks at other scattered energies. A weak feature at 762 eV would be considered using Equation 2, with:

$$E = E_S/E_0 = 762 / 937 = 0.813,$$

$$C = \cos 130° = -0.643,$$

$$S = \sin 130° = 0.766.$$

Substituting these values into Equation 2 gives a value for M_2 of 63.7 and so the peak is due to copper.

The way in which the E_S/E_0 ratio varies with atomic weight of the surface atom and the nature of the primary ion is shown in Figure 2.
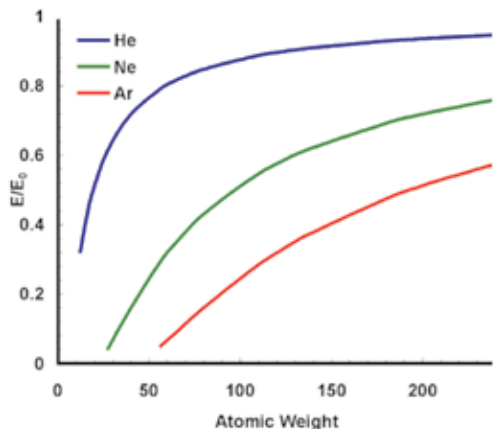

Figure 2: The variation of E_S/E_0 with atomic weight of the surface atom

ISS Spectra

Figure 3 shows ISS spectra for Cu, Ag and Au using He⁺ as the ion species. All specimens were mildly etched to remove most of the carbon and oxygen contaminants. Copper and silver ISS spectra show some residual oxygen presence around 400 eV KE. The Ag spectrum also shows some structure around 60 eV. The low KE region of ISS corresponds to sputtered ions of Ag, which contribute to a high intensity, low kinetic energy spectrum from 0 to 200 eV KE.
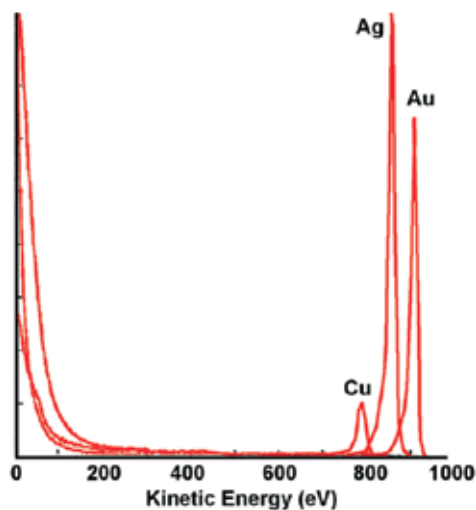

Figure 3: ISS spectra from Cu, Ag and Au, using He⁺ ions of 970 eV energy and a scattering angle of 130°

Choice of Primary Ions

Noble gases are usually used for the primary ions in ISS. This avoids contamination of the surface which would occur if a more reactive material were to be used.

From the above equations, it is clear that the only surface atoms that can be detected are those having a greater mass than the primary ions. Helium, therefore, provides the widest mass range, hydrogen is the only element that cannot be detected. Figure 4 shows an ISS spectrum from a phosphor bronze sample acquired using 1 keV He ions.
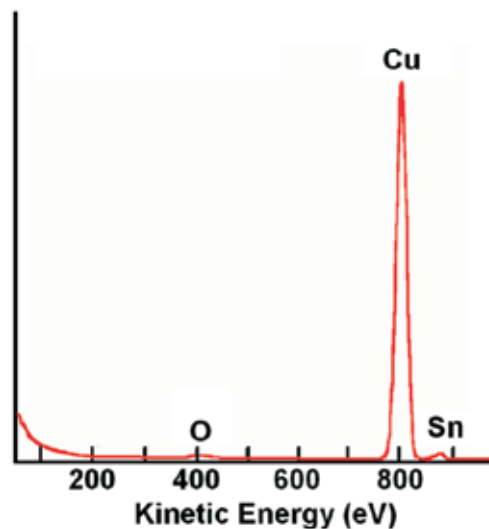

Figure 4: ISS spectrum from a phosphor bronze sample showing the presence of oxygen, copper and tin. This spectrum was acquired using He ions at 1 keV

It is clear from this figure, and from Figure 2, that the separation of mass decreases with atomic weight. Thus, in Figure 4, there is an energy separation of about 400 eV between O and Cu but less than 100 eV between Cu and Sn despite the fact that the mass difference between Sn and Cu is much greater than that between Cu and O.

If better mass resolution is required, then it is necessary to use a noble gas ion which is as heavy as possible while still being lighter than the target atoms. Using argon ions, for example, on the same sample as that shown in Figure 4 can provide sufficient mass resolution to distinguish between the two copper isotopes, Figure 5.
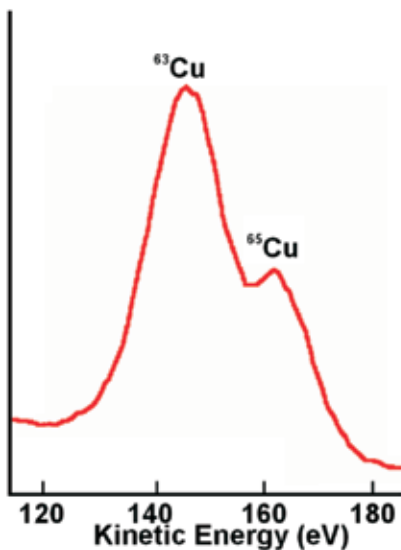
Figure 5: ISS spectrum from the same phosphor bronze sample shown in Figure 4. This spectrum was acquired using Ar ions at 1 keV and allows the two copper isotopes to be distinguished

Mass Resolution

Helium as an ion species for ISS enables elemental composition to be determined, however unit mass resolution is lost for all target atoms heavier than Na due to the physics of the scattering process. Inherent FWHM of peaks near E_0 usually are 2% of E. In general, mass resolution decreases rapidly with increasing mass.

Mass resolution also depends upon the range of angles over which ions are collected. While the survey spectrum shown in Figure 4 was obtained using a collection angle of 20°, this had to be reduced to about 3° to obtain the spectrum in Figure 5

The energy spread in the ion beam will also affect mass resolution as will the degree of collimation of the beam.

Keywords
Surface Analysis, ISS, LEIS, XPS, Surface Sensitivity

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