

Secondary Ion Mass Spectrometry

SIMS is a surface analytical technique that employs ion beam for sputtering and analyzes the masses of the ions of interest that are among the sputtered particles. In SIMS, primary ions (Cs^+ , O_2^+ ...) of energy in the range 1 to 20keV are used to sputter the specimen surface. The ions used for sputtering are called primary ions and the ions that are sputtered are called secondary ions. Since the masses of the secondary ions are analyzed, the technique is known as Secondary Ion Mass Spectrometry (SIMS).

When an ion of a few keV energy strikes at a specimen, a cascade of collisions happens in the near surface region of the specimen. When a particle (atom, cluster of atom, etc...) of the cascade with sufficient energy intercepts the surface, it is ejected out. While being ejected the sputtered particle can lose or gain electron(s) (ionized) to some extent by the collision process and mostly by electron exchange with the surrounding matrix in the surface depending on the electron affinity and ionization potential of the ejected particle and those of the matrix. The sputtered particles that have thus been ionized are analyzed by a mass analyzer and detected.

In SIMS, the sensitivity is as high as sub ppb levels. But the difficulty is in quantifying the signal. The signal suffers from matrix effect. The secondary ion intensity measured, I_s^q (counts/sec) of an analyte in the charged state q is given by the equation,

$$I_s^q = I_p Y \alpha C T$$

Equation -1

where I_p is the primary ion current, Y is the sputter yield defined as the number of secondary analyte particles sputtered by one primary particle, α is the ionization probability for the sputtered analyte to the charge state q , C is the atom fraction of the element that is analyzed and T is the ion transmission efficiency of the instrument from the specimen through various lenses, mass analyzer, apertures, etc... up to the detector. The product αT is referred to as the useful yield that is the number of analyte particles detected per analyte particle sputtered.

Sensitivity

EM can measure low count rates as low as 1c/s. Detection of 10c/s is fairly free from noise. Y can vary from $\sim .5$ to ~ 5 (typical values according to sputtering rate tables) and α varies from less than 10^{-1} to $\sim 10^{-6}$ (from tables). Primary ion column can provide currents of magnitude from pA ($\sim 10^7$ c/s) to μ A (10^{13} c/s). Under the most favorable condition (max values of these quantities) the RHS of equation becomes $10^{13} * 5 * C * 1$. The LHS can be as low as ~ 10 c/s. Thus the minimum C that can be detected under such favorable conditions becomes $10/5 * 10^{13} = 2 * 10^{-13}$. But under practical conditions, this limit can be $\sim 10^{-6}$ to $\sim 10^{-10}$ that is part per million to sub part per billion.

Depth profiling

The sputtered ions are collected, mass analyzed and counted. The counts of various masses of interest are recorded as a function of the time of sputtering. The focused primary ion beam is rastered over a square area to produce a flat crater bottom. The depth of the crater is measured using a surface profile measuring system (stylus technique or optical interference techniques). The measured depth is used to convert the sputtering time to sputtered depth.

Since this is a mass spectrometer, this can be used to get information about all elements and their isotopes and their clusters of mass within the mass analyzing capability of the analyzer. In AES the lightest atom detectable is Li and the Auger electron intensity decreases with atomic number. The sensitivity of this technique is in the percentage range which is very low compared to that of SIMS. But the advantage here is the quantification of the signal. This signal can be quantified with a standard matrix independent sensitivity factor.

Y and α are measured with homogenous standard specimens after sufficient sputtering that the sputtering process has stabilized (i.e. DRF has stabilized and incorporation of sputtering particles in the specimen has saturated). With heterogeneous specimens sputter mixing also has to be considered in quantifying the signal. Sputter mixing and matrix dependant ion yield together modify the SIMS depth profile. Hence Equation -1 cannot be directly applied to quantify depth profiling of heterogeneous specimens because sputter mixing is not included in it. Sputter mixing is represented by the convolution equation, Equation -2

$$I(z) = \int_{-\infty}^{\infty} f(z') g(z-z') dz' + v(z)$$

Equation -2

Quantification

A matrix can be considered to be homogenous when the variation of its composition remains within the limit that there is no variation of Y and α with concentration. When analyzing such homogenous specimens, the SIMS signal I can be quantified easily with the sensitivity factor SF determined with a matrix matched standard to give the concentration C .

$$C = SF * I$$

Equation -3

Another way is to measure the sensitivity of the analyte in a standardized sample with reference to the sensitivity of another species of the specimen and use it for quantifying the analyte signal of an unknown specimen. This sensitivity factor is called as relative sensitive factor (RSF). If I_E is the secondary ion intensity of the analyte E and I_R is that of a reference species

$$I_E = I_p Y_E \alpha_E C_E T$$

Equation -4

$$I_R = I_p Y_R \alpha_R C_R T$$

Equation -5

where the suffixes E and R refer to element of interest and the reference species. The ratio of these two intensities is

$$\frac{I_R}{I_E} = \frac{I_p Y_R \alpha_R C_R T}{I_p Y_E \alpha_E C_E T} = RSF \frac{C_R}{C_E}$$

Equation -6

RSF is the Relative Sensitivity Factor related to the basic secondary ion emission parameters, Y and α and the instrument transmission T as

$$RSF = \frac{Y_R \alpha_R T_R}{Y_E \alpha_E T_E}$$

Equation -7

Since the ionization probability of most of the species is below 5%, more than 95% of them are sputtered as neutrals. Hence measurement of the sputtered neutral intensity can give more quantitative results. This technique is known as Secondary Neutral Mass Spectrometry (SNMS). Here the sputtered neutrals are post-ionized and then mass analyzed as in SIMS.

The problem of quantification in SIMS arises from the matrix dependence of Y and α . Y has slight matrix dependence (variation by about one order of magnitude) and α has strong matrix dependence (varies by nearly 6 to seven orders of magnitude). This is because ionization happens when a particle leaves the surface and depending on the characteristics of the matrix at the surface the ionization probability can vary by such large extents. (Although the atoms in the sub surface cascade can get ionized they can also get neutralized within the matrix.) Since the sputtered surface is largely covered by the primary particles the SIMS signal has a strong dependence on the selection of primary probe species. Historically this was the reason for introducing oxygen probe in place of argon because oxygen has a high electron affinity and hence it can result in a strong and positive secondary ion yield and thereby reducing the matrix effect also. The matrix effect is reduced because the ionizing nature of the surface is dominated by that of oxygen that is supplied uniformly throughout sputtering. Similarly Cs probe was introduced as oxygen's counterpart because of its small ionization potential (3.893eV) to get strong negative ion yield. The Cs ion shall easily donate an electron to the sputtered electronegative particle making the sputtered particle negatively ionized. However nowadays Cs is used for both positive and negative ion detection because of the quantitative nature of the Cs complex ($Cs_n X^+$) species signal. Here X refers to any species, (electropositive, electronegative, inert atoms, clusters...). The complex species is formed by the combination of the cesium atom (or its cluster) and the species X in the ejection process and also has a high ionization probability because of the low ionization potential of Cs. The Cs complex signal depends on the combination probability that depends on the affinity between the combining species, Cs and the analyte and the ionization probability of the complex species that is dominated by that of Cs which is high. Hence the quantified nature of the Cs complex SIMS is found to be comparable to that of SNMS. Usage of a single probe (Cs) for both

electropositive and electronegative species avoids the difficulties of switching the probe. However oxygen for electropositive species and Cs for electronegative species can be used when high sensitivity is required because of the low concentration of trace elements.

The SIMS Instrument

The secondary ion mass spectrometer used in this study is the CAMECA make ims4f model SIMS instrument. The SIMS instrument has one duoplasmatron ion source to produce O_2^+ , O^- and Ar^+ ions and one Cs micro-beam ion source to produce Cs^+ ions. The gaseous ions can be accelerated to have energy from 6keV to 17.5keV. The Cs^+ ions can be accelerated to have 10keV energy. The primary ion column has electrostatic lenses to focus the ion beam on the specimen (from $50\mu m$ to submicron diameters depending on the ion current) and electrostatic deflectors to align the beam in the column and raster the focused beam on the specimen over $0\mu m \times 0\mu m$ to $500\mu m \times 500\mu m$ area. The primary ion column is at an angle 30° with respect to the normal to the specimen surface. The specimen is kept at a potential S , +4.5kV or -4.5kV to extract positive or negative secondary ions respectively. If the primary ion accelerating potential is P (kV), then the ions will have energy $(P-S)$ keV while reaching the specimen surface. The angle θ of the ion beam with respect to the specimen normal gets modified from 30° as given by the following relation.

$$\tan \theta = \sqrt{\frac{P}{3P-4S}}$$

Equation -8

The extracted secondary ions are taken through the secondary ion column that has the double focusing mass analyzer and electrostatic lenses and deflectors. There are two apertures before the electrostatic analyzer (E.S.A.) one field aperture and a contrast aperture. The size of the field aperture determines the area of the specimen from which the sputtered ions are analyzed. It is chosen such that the ions coming from the walls of the crater are not collected to improve the depth resolution, since the wall contains atoms from shallower depths. The size of the contrast aperture can be selected to modify the intensity of the ions detected and the image resolution of the secondary ion column. The mass analyzed ions are detected by a secondary electron multiplier (1count/s to 10^6 counts/s) or a faraday cup (10^4 to 10^9 counts/s).