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INSTRUMENTS LIMITED

## A An Introduction to Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is the phenomenon of secondary ion emission and the mass analysis of charged particles from solid surfaces.

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## A.1 History

The origins of SIMS can be traced back to the early part of the last century and the discharge tube experiments of J.J. Thomson, who was the first person to investigate the effects of positive ions on a metal plate.

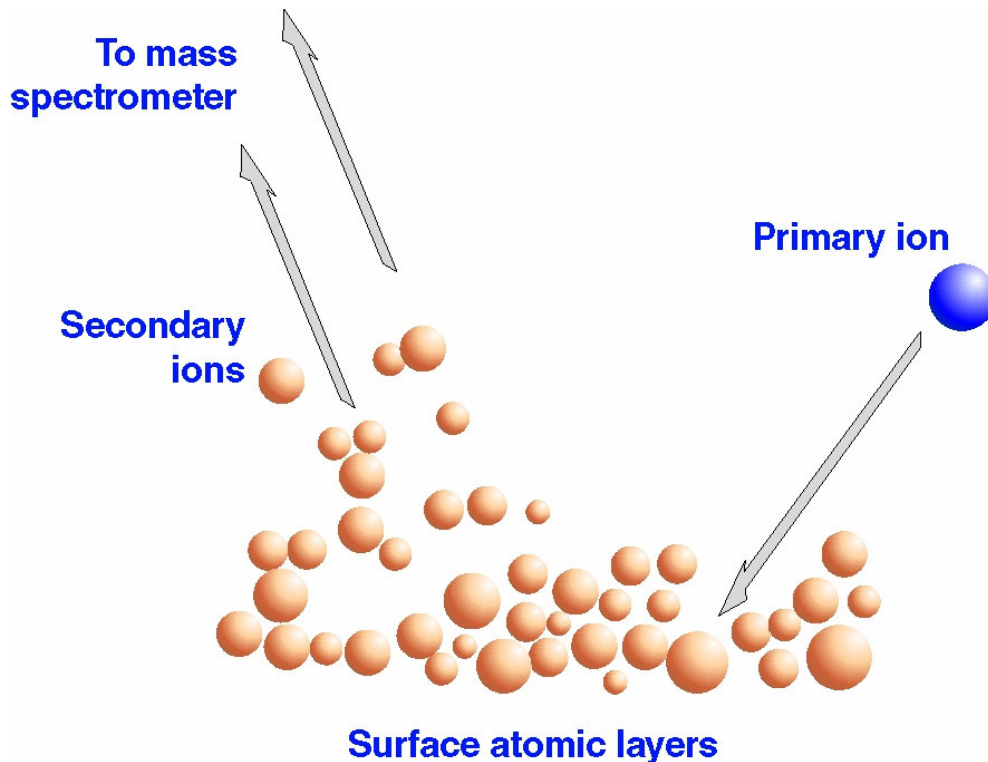
The first SIMS analytical instruments were built in the late 1940s by Herzog and co-workers, and SIMS was used in the 1960s to analyze the spatial and isotopic distribution of all the elements from hydrogen to uranium present in samples of moon rock brought back to earth. This three dimensional bulk analysis methodology has been developed and exploited intensively for semiconductor/microelectronics requirements. It has come to be known as dynamic SIMS because the surface under investigation is constantly changing.

Also during the late 1960s Benninghoven and co-workers introduced a variant which set out to perform monolayer analysis by using conditions which cause negligible surface damage. This approach is known as static SIMS because the surface under investigation remains essentially unchanged. It is most powerful in the study of organic molecules on surfaces.

Both variants really only represent extremes of the possible analysis with SIMS, as will be described below.

## A.2 The SIMS Process

In a SIMS analysis, the sample is bombarded with a beam of charged particles with energies in the 1-25 keV range. These incoming particles are called primary ions. In the MiniSIMS, gallium ions ( $\text{Ga}^+$ ) with an energy of about 6 keV are used as the primary ion beam.



The primary ions deposit energy into the surface layers. Around the impact site and to the depth of ~3 nm, many bonds are broken and there is much random displacement and movement of atoms. This region is called the collision cascade. Collisions which result in translational energy being directed back to the surface layer lead to ejection of material. This process is termed sputtering of the surface.

The sputtered material is mostly ejected as neutral fragments, but ~1% is ejected in the form of charged particles. These are known as secondary ions, and the vast majority are singly charged. Both positive and negative ions are emitted, and they range in size from single atoms to very large clusters of atoms (molecular ions and fragments). Sputtered ions can leave the surface some distance (up to ~ 5 nm) from the impact site. As a broad generalization, as this distance increases the more likely is the desorption of the larger fragment ions since these need to have the minimum of internal energy to prevent disintegration.

Typically, secondary ions have kinetic energies of the order of 20 eV, but different ions have different energy distributions. In particular the molecular/cluster ions have significantly narrower distributions than atomic ions and they peak at slightly lower energy.

Under typical SIMS conditions most of the sputtered material (>95%) emanates from the uppermost two atomic layers, so the sampling depth can be taken to be ~1 nm. Large organic fragments are more likely to come predominantly from the surface monolayer, whilst the most energetic atomic fragments may come from significantly deeper layers.

Primary ion bombardment also causes the emission of low energy electrons and these can be detected to provide sample visualization (topographic information) in a manner analogous to a Scanning Electron Microscope (SEM).

The secondary mass spectrum is obtained by collecting the secondary ions and subjecting them to mass filtration prior to detection. Three types of mass filter (or mass analyser) are used in SIMS - magnetic sector, quadrupole and time-of-flight; the MiniSIMS uses a quadrupole mass filter. Since this device cannot filter ions with high kinetic energy, it requires an energy filter to select the appropriate fraction of the secondary ion energy distribution prior to mass analysis. Positive and negative secondary ion mass spectra are obtained in sequential experiments by switching the polarity of the whole mass spectrometer.

The mass filter must be capable of separating secondary ions that differ in mass by one atomic mass unit (amu or dalton) over the whole mass range. The mass resolution or resolving power ( $R$ ) of the mass spectrometer is given by

$$R = m/\Delta m$$

where  $m$  is the mass of the detected species and  $\Delta m$  is the peak width.  $\Delta m$  is often quoted as the full width at half maximum peak height (fwhm) but in the case of the quadrupole it is more useful to quote  $\Delta m_b$ , the full width at 10% maximum peak height i.e. the width at the base of the peak. In the MiniSIMS the quadrupole is set up to give  $\Delta m_b \sim 1$  for all  $m$ , hence  $R \sim m$ .

The secondary ion current  $I_s$  for a selected ion of mass  $m$  (or more correctly of mass/charge ratio  $m/z$ , where  $z$  is almost always unity in SIMS) is given by

$$I_s(m) = I_p \cdot y \cdot \alpha \cdot T \cdot C(m)$$

where  $I_p$  is the primary ion current,  $y$  is the sputter yield,  $\alpha$  is the ionization probability,  $T$  is the overall transmission of the energy and mass filters (i.e. the fraction of the sputtered ions of a given mass which are actually detected), and  $C(m)$  is the concentration of the detected species in the sputtered volume.

For a quadrupole set up as described above,  $T$  is of the order 0.1% and is approximately inversely proportional to  $m$ . Therefore the sensitivity of the instrument decreases as higher mass ions are selected by the mass filter.

$y$  is the total yield of sputtered particles, neutral and charged, of mass  $m$  per incident primary ion;  $y$  is typically between 1 and 20 for atomic species and it is a function of the mass and energy of the primary ion and its angle of incidence (peaking strongly at  $\sim 60^\circ$  to the surface normal). Under the constant primary beam conditions in the MiniSIMS,  $y$  only varies by a factor of 5 for different elements.

$\alpha^+$  and  $\alpha^-$  are the respective probabilities that the sputtered particle will be a positive or negative ion. Ionization probabilities vary dramatically across the elements and are additionally very sensitive to the electronic state of the surface. The secondary ion yield ( $y\alpha$ ) can therefore vary by over four orders of magnitude for different elements and may be very matrix sensitive. For example, the yield of  $Mg^+$  from clean Mg versus MgO is 0.01/0.9 (= 0.01) whereas the yield of  $W^+$  from clean W versus  $WO_3$  is 0.00009/0.035 (= 0.003).

In summary:-

	Definition	dependence on species $m$	dependence on matrix
$I_p$	primary ion current	none	none
$T$	instrumental transmission	low	none
$y$	sputter yield (atoms ejected per incident ion)	medium	low
$\alpha$	probability of ionization (to form secondary ion)	high	high

SIMS is therefore inherently non-quantitative, i.e. there is no simple *a priori* relationship between concentration of a given mass  $C(m)$  and peak intensity,  $I_s(m)$ . However, for a given elemental species in a fixed matrix, and provided the concentration range is not too great, the intensity ratio of the elemental peak to that of a matrix-related peak will usually follow a linear relationship with concentration. This allows composition to be determined if a suitable standard calibration material is available. Such measurements are routine for dopant elements in semiconductor materials (e.g. B in Si) and critical to the microelectronics industry.

### A.3 Different Types of SIMS Analysis

SIMS is a versatile technique, giving 3-dimensional information about the surface and near surface region of a material. It can be used for surface analysis (static SIMS), highly sensitive bulk analysis (dynamic SIMS), analysis of concentration variations with depth below the surface (depth profiling) and analysis of lateral heterogeneity (microanalysis and imaging i.e.

chemical microscopy).

In static SIMS (SSIMS) the aim is to minimize damage to the sample surface during data acquisition through the use of a very low primary ion current density ( $<1 \text{ nA cm}^{-2}$ ). If the total primary ion dose can be limited to between  $10^{12}$  and  $10^{13}$  incident ions  $\text{cm}^{-2}$ , then the spectrum will be representative of essentially virgin material in the uppermost one to two monolayers of the surface. This is particularly useful for identifying the molecular structure of organic species on the surface through the characteristic pattern of their specific fragment ions.

Conversely, in dynamic SIMS (DSIMS), the primary ion current density is set as high as possible in order to maximize secondary ion yields. The sample will be eroded during analysis so the spectrum, at any time, will be representative of the average composition within the sampled volume. Sensitivity to trace elements in the bulk is optimized in this mode.

Depth profiling is a more sophisticated variant of DSIMS. A concentration profile for a chosen element can be measured by tuning the mass filter to an appropriate value of  $m/z$  (+ or -) and recording the peak intensity continuously as a function of sputtering time. Rapid switching between masses means that a number of peaks can be monitored at effectively the same time. Alternatively, after a chosen sputtering time, a full mass spectrum can be recorded (possibly with a reduced beam current) and the cycle repeated. A means of calibrating the erosion rate is required in order to convert the sputtering time into a depth scale, and this is usually done by physical measurement of the final depth of the resultant crater at the end of the analysis.

In the microscopic mode, the primary ion beam is focused to a small spot (from 0.1 mm to 0.1  $\mu\text{m}$  in diameter). This means that a microanalysis can be performed for an area of similar dimensions at a specific point on the sample. Alternatively the focused beam can be rastered (digitally scanned) from point to point (pixel) over a limited area with the mass filter tuned to a chosen  $m/z$  value. This creates a 2-dimensional map showing the variations in intensity of that peak over the sample surface, and so the resulting image shows the location of a particular chemical species. The high sensitivity of SIMS means that images such as this can be acquired in times ranging from a few seconds to a few minutes.

The physical area of interest has usually been identified from visual examination or optical microscopy. It may also be selected *in situ* using a topographic image. This is generated in the way described above, except that the variations in intensity of secondary electrons (rather than specific secondary ions) are measured. Total ion images (obtained with the mass filter set to pass all ions) again tend to be dominated by topographic contrast and provide an alternative way to generate a physical image of the sample. In either case the utilized signal is much more intense than that for a given secondary ion; this allows imaging in quasi-real time, but of course almost no chemical information about the sample is obtained.

Imaging is, in principle, possible in both static and dynamic modes. However the requirement

for adequate image contrast will inevitably tend to increase the dose in imaging experiments; remember that an image of 200 x 200 pixels (as typically used in the MiniSIMS) requires 40,000 individual analyses.

#### **A.4 Relationship of SIMS to Other Analysis Techniques**

In the context of surface analysis, SIMS is complementary to Ion Scattering Spectroscopy (ISS), X-ray Photoelectron Spectroscopy also known as Electron Spectroscopy for Chemical Analysis (XPS or ESCA), Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES). These are discussed in detail in the Appendix.

Against this backdrop of related techniques, the main features of SIMS can be summarized as follows:-

Surface specificity is very high (approaching the ultimate set by ISS) and greater than for XPS, AES and XRF.

Elemental sensitivity is also greater and can be of the order of ppm of a monolayer, whereas XPS, AES and XRF have sensitivities ~ 0.2 atomic percent.

XPS and AES do not detect hydrogen, and XRF has zero or poor sensitivity to Lithium, Beryllium and Boron, whereas SIMS can detect all the light elements. SIMS also has the advantage of isotope specificity.

The pattern of SIMS cluster ions contains a great deal of molecular/structural information for both organic and inorganic surfaces.

Total secondary ion images contain topographic contrast and provide surface visualization, as in SEM but with lower spatial resolution.

Mass resolved images give chemical contrast and allow element mapping, as in XPS, AES or EDX, but the high sensitivity of SIMS means imaging is faster.

Shallow depth profiling is straightforward because the same ion gun is used for both erosion and analysis.

The main drawback to SIMS is that quantification is difficult except for the specific case of trace concentrations with calibration standards.

Further reading.

For a basic text on the principles of surface analysis techniques see:

*Surface Analysis: The Principal Techniques*,  
Ed. J. C. Vickerman, Wiley, Chichester (1997)

For a more wide ranging book text on chemical analysis of materials, including electron microscopy and related techniques see:

*Structural and Chemical Analysis of Materials* by  
J.P. Eberhart, Wiley, Chichester (1991)

For a more detailed treatment of XPS, AES, ISS and SIMS and their applications see:

*Practical Surface Analysis Second Edition, Vol. 1: Auger and X-ray  
Photoelectron Spectroscopy; Vol. 2: Ion and Neutral Spectroscopy*,  
Eds. D. Briggs and M.P. Seah, Wiley, Chichester (1996)

For a more detailed treatment of Electron Microscopy including XRF, EDX & WDX see:

*Electron Microscopy and Analysis (3<sup>rd</sup> Edition)*  
Ed. P. Goodhew, J. Humphreys & R. Beanland Taylor & Francis (2001)

## **Appendix - Related Surface Analytical Techniques**

In Ion Scattering Spectroscopy (ISS) a low energy (5 keV) ion beam bombards the sample and scattered primary ions are energy analyzed at a chosen scattering angle. For a given angle/primary ion mass combination there is a simple relationship between the atomic number,  $Z$ , of the scattering atom and  $E/E_0$ , where  $E$  is the measured, scattered ion energy and  $E_0$  the primary ion energy. Hence peaks in the energy spectrum correspond to the different elements.

Primary ions are rarely scattered without being neutralized from layers below the uppermost atomic layer. Such ions are therefore not detected, making ISS is the most surface sensitive analysis technique. However, scattering from H is very weak so surface hydrocarbon contamination can easily suppress the expected spectrum. Resolution of elements with adjacent atomic numbers across the periodic table requires more than one experiment since the primary ion mass needs to be changed to optimize resolution in different regimes of  $Z$ . ISS data can be quantitative, but overall the technique is not a popular choice for routine surface analysis.

The dominant surface analysis techniques for practical analysis are the electron spectroscopies X-ray Photoelectron Spectroscopy also known as Electron Spectroscopy for Chemical Analysis (XPS or ESCA), and Auger Electron Spectroscopy (AES).

In XPS the sample is bombarded with soft X-rays, which leads to emission of photoelectrons from the atomic (core) and valence levels. Those emitted close to the surface can escape without energy loss, according to the equation

$$E_K = h\nu - E_B - \phi$$

where  $E_K$  is the kinetic energy,  $h\nu$  is the X-ray energy,  $E_B$  the electron binding energy in the solid and  $\phi$  the sample work function.

$E_K$  is measured by the electron spectrometer, allowing  $E_B$  to be determined. This is specific to the atomic shell involved, and with the X-rays used ( $h\nu < 1.5$  keV) at least one core level is excited for all elements except hydrogen. The sampling depth is dependent on  $E_K$  and therefore varies with the level being detected, but it falls in the range 2 - 10 nm under typical conditions. XPS is inherently quantitative and peak areas can easily be transformed into relative atomic concentrations.

For any given core level the value of  $E_B$  varies within small limits as a function of chemical state (e.g. oxidation states or organic functionality) and these “chemical shifts” of the peaks in the spectrum can be analysed to give valuable structural information. Depth profiling can be achieved by cyclical experiments involving sputtering with an auxiliary ion gun, or by angle resolved experiments. Imaging and microanalysis can be achieved by either microprobe approach (i.e. focused X-ray source) or by a microscope approach (i.e. spatial relationships are preserved during filtration in the electron spectrometer). In both cases the spatial resolution can be  $< 10 \mu\text{m}$ , with microanalysis possible from regions about  $50 \mu\text{m}$  in diameter.

It is most convenient to consider Auger Electron Spectroscopy (AES) in the context of electron microscopy and related techniques. In Scanning Electron Microscopy (SEM) the sample is bombarded with a finely focused electron beam, typically with energy 10-30 keV. Low energy secondary electrons emitted close to the surface give rise to the familiar topographical image of an SEM. Backscattered primary electrons, which are much more energetic, are detected from deeper into the solid. The scattering efficiency is a function of atomic number  $Z$ , giving rise to contrast changes between different elements.

The primary electrons also cause core-shell ionization (as do the X-rays in XPS). The resulting core-hole can relax in two ways. In both processes the first step is for a less tightly-bound electron to drop into the core-hole. The difference in energy between the two levels involved is then dissipated by either emission of an X-ray (X-ray Fluorescence (XRF)) or by emission of an electron (AES).

In the XRF process the emitted X-ray photon has an energy which is the difference between

the two energy levels involved and which is characteristic of the atom originally ionized. X-rays can be analyzed in terms of energy or wavelength. On an SEM instrument this analytical facility is referred to as Energy Dispersive analysis of X-rays (EDX or EDS) or (less commonly) Wavelength Dispersive analysis of X-rays (WDX). Peak intensity in the X-ray spectrum is easily quantified to give atomic composition. However, this information comes from up to several microns below the surface and limitations in sensitivity mean that the useful lateral resolution is about 1  $\mu\text{m}$ . The lighter elements ( $Z < 6$ ) give weak or nonexistent XRF intensity.

In the Auger emission process the energy level difference is dissipated by emission of a second (Auger) electron with the appropriate kinetic energy  $E_A$ . Very approximately, this energy is given by

$$E_A = E_1 - E_2 - E_3$$

where  $E_1$ ,  $E_2$  and  $E_3$  are, respectively, the energies of the initial core level, the less tightly bound level and the original level of the Auger electron. Since all 3 levels are characteristic of the atom, the energy of the Auger electron can be used to identify the element.

For the lighter elements, Auger emission dominates over XRF. The Auger spectrum is obtained by electron energy analysis, as in XPS, and peak intensities are readily quantified to give atomic composition. To be detected, Auger electrons must be emitted close to the surface, so the sampling depth is of the same order as that for XPS. Auger electron spectroscopy (AES) can be carried out on an SEM provided it has a ultra high vacuum compatible vacuum system, but it is more usually carried out on a dedicated instrument. Spatial resolution in imaging can be very high ( $< 0.1 \mu\text{m}$ ) but electron beam damage and/or charging effects effectively prevent the analysis of organic surfaces. Depth profiling with simultaneous ion beam sputtering and detection of specific Auger electrons is routinely used.