The technique of Secondary Ion Mass Spectrometry (SIMS) is the most sensitive of all the commonly-employed surface analytical techniques - capable of detecting impurity elements present in a surface layer at < 1 ppm concentration, and bulk concentrations of impurities of around 1 ppb (part-per-billion) in favorable cases. This is because of the inherent high sensitivity associated with mass spectrometric-based techniques.

There are a number of different variants of the technique:

- **Statics SIMS**: used for sub-monolayer elemental analysis
- **Dynamic SIMS**: used for obtaining compositional information as a function of depth below the surface
- **Imaging SIMS**: used for spatially resolved elemental analysis

All of these variations on the technique are based on the same basic physical process and it is this process which is discussed here, together with a brief introduction to the field of static SIMS. Further notes on dynamic and imaging SIMS can be obtained in Section 7.4 - SIMS Imaging and Depth Profiling.

In SIMS the surface of the sample is subjected to bombardment by high energy ions - this leads to the ejection (or sputtering) of both neutral and charged (+/-) species from the surface. The ejected species may include atoms, clusters of atoms and molecular fragments.

In traditional SIMS it is only the positive ions that are mass analyzed - this is primarily for practical ease but it does lead to problems with quantifying the compositional data since the positive ions are but a small, non-representative fraction of the total sputtered species. The displaced ions have to be efficiently extracted from the sample region and subject to energy-filtering before they are mass analyzed (so that only ions with kinetic energies within a limited range are mass analyzed).

The mass analyzer may be a quadrupole mass analyzer (with unit mass resolution), but magnetic sector mass analyzers or time-of-flight (TOF) analyzers are also often used and these can provide substantially higher sensitivity and mass resolution, and a much greater mass range (albeit at a higher cost). In general, TOF analyzers are preferred for static SIMS, whilst quadrupole and magnetic sector analyzers are preferred for dynamic SIMS.

The most commonly employed incident ions (generically denoted by \( I^+ \) in the above diagram) used for bombarding the sample are noble gas ions (e.g. \( \text{Ar}^+ \)) but other ions (e.g. \( \text{Cs}^+ \), \( \text{Ga}^+ \) or \( \text{O}_2^+ \)) are preferred for some applications. With TOF-SIMS the primary ion beam is pulsed to enable the ions to be dispersed over time from the instant of impact, and very short pulse durations are required to obtain high mass resolution.
Static SIMS

In static SIMS (SSIMS) the aim is to obtain sufficient signal to provide a compositional analysis of the surface, without actually removing a significant fraction of a monolayer. This requires the use of very low ion fluxes (around $10^{12}$ cm$^{-2}$) to ensure that each ion is statistically-likely to impact upon fresh, undamaged surface and that the sputtered secondary ions are representative of the original surface, rather than surface that has already been "damaged" by earlier ion impacts. In this form, the technique is capable of providing information about adsorbed molecular layers or the topmost atomic layer of the solid surface.

Example: Polytetrafluoroethylene (PTFE)

The static SIMS spectra from the surface of PTFE (polytetrafluoroethylene)

Note the substantial differences between the positive and negative ion spectra. In each case the most intense peaks correspond to relatively stable positive and negative ions respectively.
External Sites

- Time-of-Flight (TOF) Mass Spectrometry

Contributors

Roger Nix (Queen Mary, University of London)