SIMS without sums

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Secondary Ion Mass Spectrometry (SIMS) is probably the most powerful analytical technique for the characterization of semiconductor materials. Its strength lies in its ability to perform high sensitivity chemical analysis directly on semiconductor materials with high spatial and depth resolution. As part of the continuing series on assessment techniques, *III-Vs Review* presents a mathematics- free overview of the process.

The basic principles behind Secondary Ion Mass Spectrometry (SIMS) are simple. To put it crudely, SIMS is nothing more than sand blasting on an atomic scale. A beam of energetic ions is fired at the sample surface and atoms and molecules are sputtered off the surface into the vacuum that surrounds the sample. The whole SIMS process takes place in a vacuum system, as do many of the deposition and etching processes used in device fabrication. Indeed, SIMS has much in common with fabrication techniques like ion implantation and reactive ion etching.

So, a well-defined beam of ions is fired at the sample and knock atoms and molecules off the surface. This etches away the part of the sample that the beam is aimed at, but what of the material that comes off? Most of the sputtered particles are neutrals, that is they have no electric charge and are of no interest, but some leave the surface of the sample in the form of ions, either positively or negatively charged, and it is these ions that constitute the analytical signal. From the mass of the ions the chemical (isotopic) species that gives rise to the signal can be easily determined. By using a mass spectrometer to weigh the ions, the information on what atoms are present in the sample is revealed. Things get a little more difficult, but not impossible, to interpret when the ions come off in the form of molecules rather than atoms as will be shown later

Static or dynamic?

SIMS has evolved into two distinct sub-sets, Static SIMS (SSIMS) and Dynamic SIMS (DSIMS). These perform quite different analytical tasks and should not be confused with each other, although both have their role to play in semiconductor characterisation. SSIMS is all about the chemical - molecular- composition of the outermost monolayer of the sample surface. DSIMS is the more familiar version of SIMS in the semiconductor context, producing the ubiquitous dopant depth profiles that are often seen in III-Vs Review. Curiously, in recent years there has been something of a reunion of these two branches of SIMS as instruments configured to obtain the maximum analytical signal in the Static mode are proving capable of performing high quality depth profiles of ultra-low energy implants and shallow structures.

Figure 1 shows a schematic diagram of the SIMS process. The sample is shown as an idealized piece of material composed of atoms arranged in a regular pattern. The arrangement and composition of the atoms in the surface layer may differ in both composition and arrangement to those in the bulk as a result of physical effects, such as surface reconstruction or chemical effects like oxidation. In this simple model these surface effects have been neglected.

A primary ion is produced in an ion gun where it is accelerated and directed towards the sample surface. The primary ion impacts up-
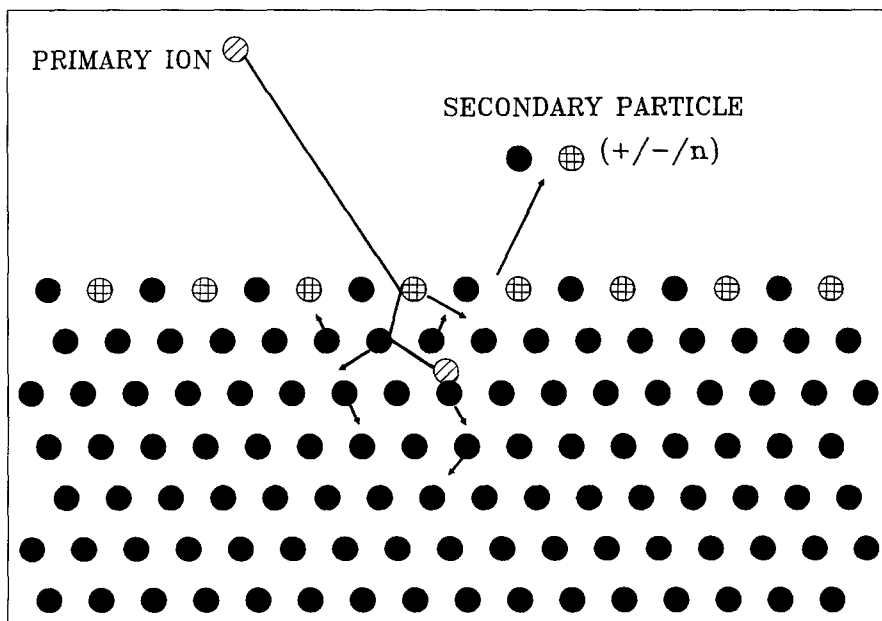

Figure 1: Schematic diagram of the sputtering process.

on the sample surface and creates a collision cascade setting the atoms in the sample in motion as it loses energy through a series of collisions. Some of energy in the cascade can be transferred in such a way that atoms or molecules in the surface layer receive enough energy to break the bonds that hold them in place causing them to be sputtered off into the vacuum. The sputtered particles can be atoms or molecules, positively or negatively charged, or, indeed, neutral species. It is important to recognise that:

1. the sputtered particle leaves the surface from a region that is physically separated from the region where the primary particle entered the surface;

2. the primary particle causes damage to the surface and sub-surface regions by breaking bonds between atoms and moving the atoms in the sample surface off their lattice sites;

3. the primary particle becomes implanted into the sample surface.

By counting the numbers of different ions leaving the sample it should be possible to determine the concentrations of the different elements present in the sample. If all elements produced the same number of ions and neutrals as a result of the sputtering process the analytical task would be easy, a simple count of the ions would give the concentrations. Unfortunately, each element produces a different fraction of ions and neutrals, some elements favouring the production of positive ions (for example, the group 1 metals), while others give predominantly negative ions (the halogens, for example). Some elements, like the rare gases, do not ionize easily in the sputtering process.

To complicate matters further, the ratio of ions to neutrals produced by any one element may

vary depending upon the chemical environment of the element. The ion yield from clean metal surfaces can be orders of magnitude less that the ion yield from the same metal when it is in an oxidized state. This is the so called SIMS matrix effect.

Rather than being a barrier to the use of the technique, these effects are exploited to facilitate the analysis. Oxygen primary ion beams are used to deliberately oxidize the sample surface during analysis (and in some cases a jet of molecular oxygen is also blown at the sample surface during the sputtering process to ensure a high level of surface oxidation). This enhances the positive secondary ion yields from electropositive elements, but does little for the electronegative species. In order to maximize the yields from these elements caesium ion bombardment is used together with negative secondary ion detection. Some elements, zinc for example, give the best analytical signal when caesium primary ion bombardment is used together with positive secondary ion detection, the zinc-caesium molecular ion being detected.

In any measurement system it is a distinct advantage if the measured parameter varies linearly with the quantity sought. In SIMS, for the measurement of dilute impurity species distributed through a uniform matrix, the analytical signal does indeed vary linearly with the concentration of the analyte. However, for higher concentrations, such as matrix element levels in compound semiconductors, it is not necessarily true that the analytical signal varies linearly with concentration.

All these quirks of SIMS give it an air of mystery and complexity, suggesting it is something of a black art that only a guru in the subject can fully comprehend. This does the technique an injustice; in capable hands it is a simple technique that is moderately straightforward to use and interpret,

without requiring a deep knowledge of the underlying physics of the process. With a set of closely matched 'standards' (reference materials) it is possible to do routine quantitative analyses and even when standards are not available qualitative analyses are often useful in a problem solving context.

Static SIMS

Much of the above discussion in reality relates to DSIMS and is discussed in more detail later on, but what of SSIMS?

Consider once again Figure 1. Before the erosion process begins the surface of the sample is undamaged and reflects the surface chemistry of the material. The first primary ion strikes the surface and initiates a collision cascade. A secondary particle then leaves the surface, this can be a single atom, either ionized or neutral, or a collection of atoms, a "molecular fragment", carrying with it information on the surface chemistry of the undamaged surface. A second primary ion then arrives, again releasing a secondary particle from an undamaged region of the surface.

So, as the erosion of the surface proceeds the probability that the secondary particle originates from an area of the surface damaged by a previous primary impact increases. This means the surface chemistry of the damaged region may no longer be characteristic of the original surface chemistry of the sample. Thus, it is clear that as the analysis proceeds the information content of the mass spectra of ions released from the surface changes. This leads to the concept of the Static SIMS limit, that is the primary ion dose above which chemical information regarding the surface cannot be relied upon. Pragmatically, the static SIMS limit is about 1% of a monolayer.

So what sort of information can Static SIMS reveal? Typically, a mass spectrum is recorded from the surface of the sample from which the
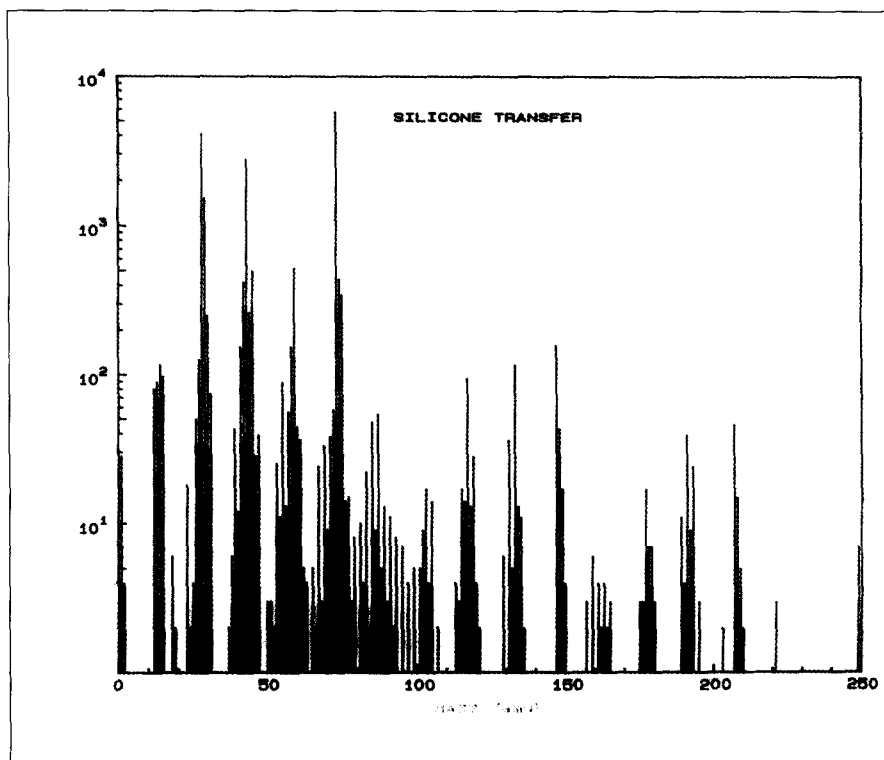
Figure 2: Static SIMS mass spectrum of a poly(dimethylsilicone) contaminated sample.

molecular fragment peaks can be interpreted qualitatively in terms of the surface chemistry of the material or, as is more common, in terms of the surface contamination of the material — this mode of measurement is sensitive to the outer monolayer of the sample.

Figure 2 shows a typical SSIMS spectrum recorded from a layer of deliberately produced organic contamination. In this case the contaminant was poly(dimethyl silicone), a widely used material with desirable properties when used in the right place, but often producing failures when in the wrong place. The material can be recognized by the presence of mass fragments at masses 73, 147, 207 and 221, which can be directly related to the structure of the molecule. Compilations of characteristic peaks are available to assist in the interpretation of these sometimes complex spectra.

Dynamic SIMS

Compared with SSIMS, Dynamic SIMS uses a much higher primary ion beam fluence resulting in the surface of the sample being continuously eroded. Normally the primary ion beam is focussed to a spot and rastered over the sample surface to produce a square, flat bottomed crater. Secondary ions originating from the central part of the crater are used for analysis. By monitoring the intensity of selected secondary ion signals as a function of time a depth profile showing the variations in composition of the sample is produced. By calibrating the secondary ion signals against reference materials, and by measuring the depth of the sputtered crater, a quantified depth profile can be obtained.

It is important that the secondary ion signal is collected only from the central region of the crater. If secondary ions from the edge of the crater are included in the analytical signal the depth profile will have poor depth resolution. This is because information from a range of depths will be included in the measured signal, the crater edge effect. Similarly, if the base of the crater is not flat the depth profile will show poor depth resolution.

There are other more fundamental factors that can lead to poor depth resolution. One important consideration is the energy of the primary ion used to erode the sample surface. The energy imparted to the surface by the impact of the primary particle goes not only towards removal of material from the surface, it also causes relocation of atoms beneath the surface which will subsequently be exposed as the erosion proceeds. This is termed atomic mixing. The obvious way to reduce atomic mixing is to reduce the impact energy of the primary particle. This can lead to a loss of primary beam current, however, resulting in longer analysis times, an increase of primary beam spot size and other technical difficulties.

Another problem that can occur is the development of surface roughness. As the sputtering process proceeds the surface being analysed can roughen. This is not often a problem with the normal analysis of semiconductor materials, but it can be severe when analysing metallic contact layers or semiconductor material below metal overlayers. In order to overcome, or at least minimize, the effects of surface roughening sample rotation during analysis has been shown to be successful in suppressing the development of roughness. Figure 3 shows profiles of a boron implanted, 1 µm thick, aluminium film on silicon with and without sample rotation showing the improvement in depth resolution that can be obtained.

Interpreting data

With a mass spectrometry based technique like SIMS there is no background signal above which the analytical signal has to stand out (as is the case of the electron spectroscopies, XPS and Auger, or in energy dispersive X-ray analysis). Consequently, SIMS is an inherently sensitive technique. As we have seen in the discussion of SSIMS, however, there are molecu-
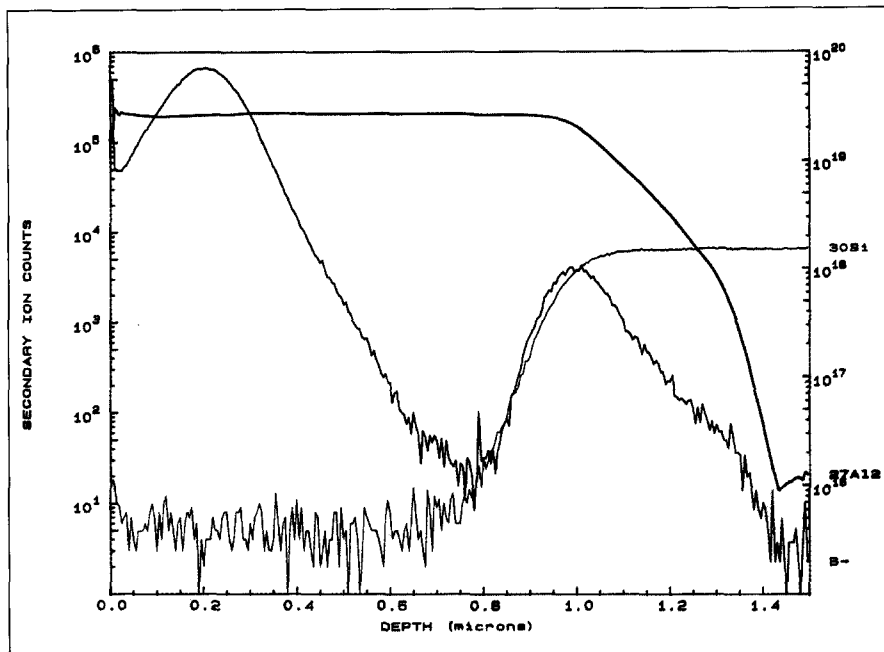
Figure 3a: Profiles for boron, aluminium and silicon through a boron implanted one micron thick aluminium film on silicon without rotation.

lar fragment peaks that can cause confusion if they have the same mass as an isotope of an element of interest. Of course, the analyst can make use of isotope patterns in order to distinguish elemental signals from molecular signals, but unfortunately some elements are monoisotopic and so this approach cannot always be used.

Indeed, the elemental signal may be lower than the interfering molecular signal, so what then?

There are two tricks that can be used here, high mass resolution and energy filtering. High mass resolution, as its name implies, exploits the fact that small mass differences exist between molecular fragments and isotopes of ele-

ments occurring at the same nominal mass. Thus by running the mass spectrometer in high mass resolution the elemental and molecular signal can be resolved, albeit at the expense of signal. Another, simpler, method of discriminating between molecular interferences and elemental signals is to use energy filtering. As molecular ions have much narrower energy distributions than do atomic ions, careful selection of the energy of the ions passing through the mass spectrometer allows the analyst to discriminate between the wanted and unwanted signals.

- One feature of a SIMS profile that often causes confusion is the surface spike. Almost inevitably when looking at a SIMS depth profile the first data points are higher at the surface than subsequent ones. This can indeed be caused by an increased concentration of those elements at the surface, but another possible cause is the transient change of sputtering rate as the surface changes from its unsputtered state to a stable condition in which the implanted primary ions have reached their equilibrium concentration and, at the same time, the surface oxide is sputtered away.

A powerful technique

This discussion of SIMS has, arguably, dwelt too much on the difficulties and problems that can arise during SIMS analysis, rather than all of the wonderful things the technique can achieve. So, in conclusion, it is certainly worth restating that SIMS is a powerful technique that, in the hands of a competent analyst aware of its traits, can provide a wealth of useful information, not just from semiconductors but from almost any solid material.

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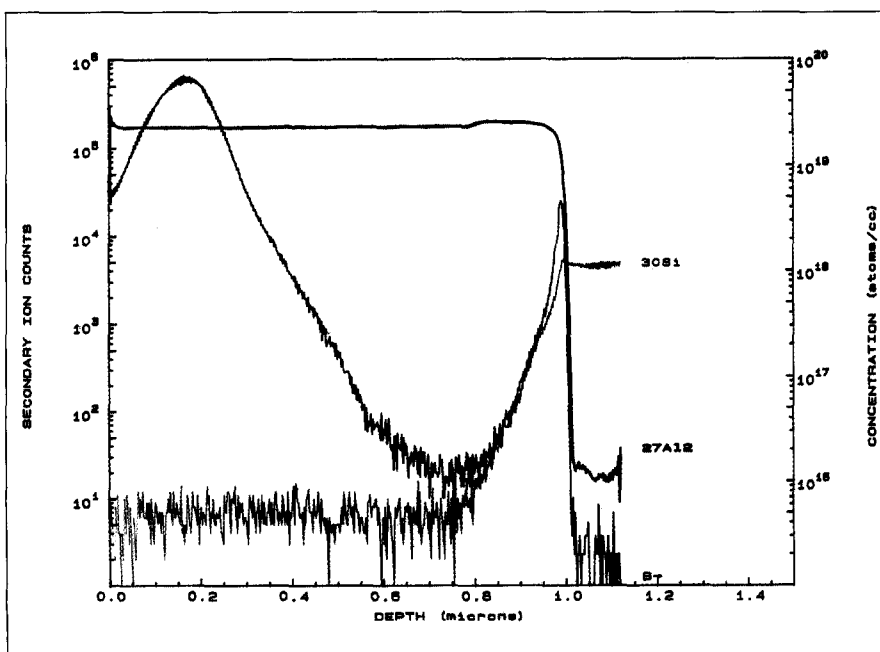E-mail: d.e.sykes@lsaltd.co.uk.

Figure 3b: Profiles for boron, aluminium and silicon through a boron implanted one micron thick aluminium film on silicon with sample rotation during analysis.