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New Tools for the Surface Engineer

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The global budget for nanotechnology research exceeded $1 billion this year. In the UK, the industries most benefiting from nanoscience and technology are health & life sciences, IT & electronics, defence & aerospace, materials, food & drink, and transport. In the development of the novel materials demanded by these industries, there is an increasing use of surface engineering to create surfaces with a specific functionality. These tailored surfaces interact with their surroundings in a particular way while leaving the bulk properties of the material such as mechanical strength unaltered. The engineering of surfaces in this way brings with it a need for surface-specific analysis techniques for use in both the research laboratory and the production facility.

This article concentrates on one such analysis technique, known as secondary ion mass spectrometry (SIMS). It introduces a desktop instrument that provides a cost effective option for surface engineers, called the MiniSIMS, a surface-analysis instrument developed by Millbrook Scientific Instruments (UK). Currently the number of SIMS instruments around the world is still relatively low, not least because of the high costs traditionally associated with the technique. An on-site SIMS analysis capability used to mean a substantial investment in terms of the capital cost of instrumentation, supporting service facilities and experienced personnel required.

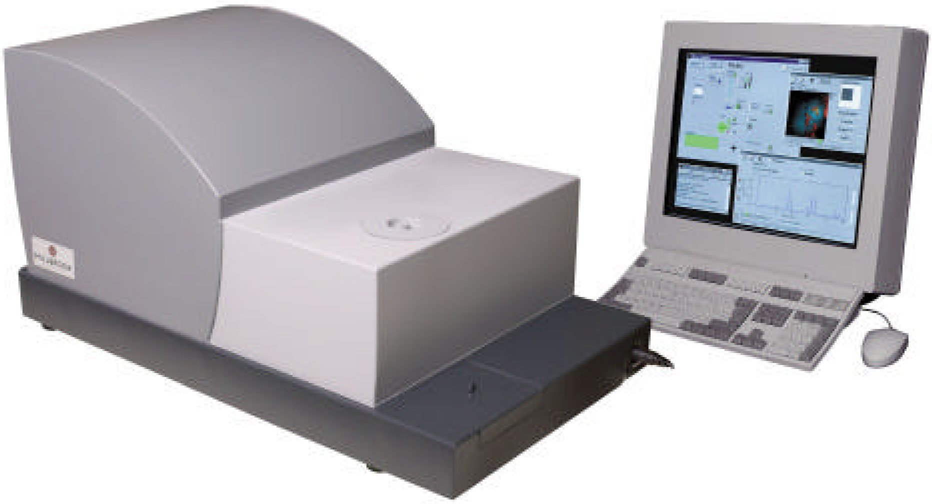

Figure 1 An example of an automated desktop surface analysis instrument – the Millbrook MiniSIMS.

Fortunately, we now have lower cost instrumentation such as the MiniSIMS [Figure 1]. Operation is straightforward via a Windows™ interface, with the computer also monitoring the instrument's performance. This type of instrumentation allows high throughput analysis by less experienced operators. It is sufficiently compact to be treated as a mobile instrument, and can be operated remotely via a modem link. This is very useful where the need for analysis is shared by several locations within a company.

This type of desktop instrumentation uses the power of the SIMS technique (which is explained below) in a form and at a price that allows its widespread use. Not surprisingly, the MiniSIMS does not offer the same ultimate performance specification as a conventional SIMS instrument, but conversely, it does provide excellent performance for the majority of applications.

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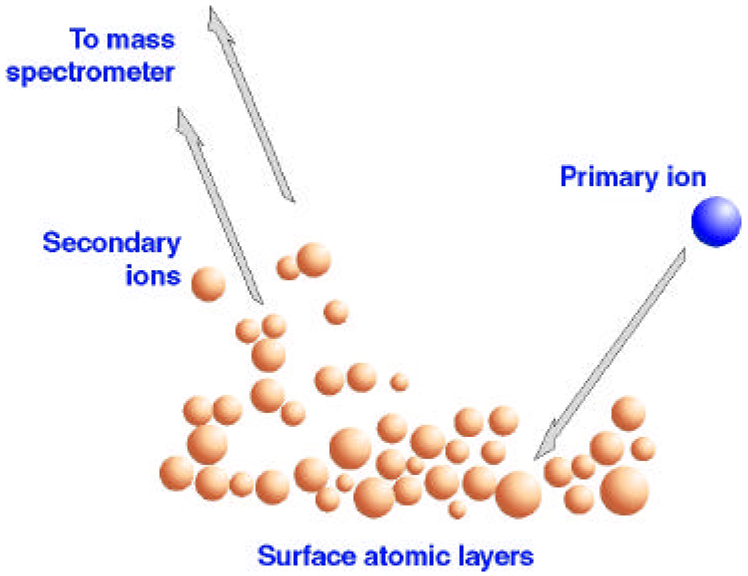

Figure 2 The SIMS process. Bombardment of the surface with high energy ions produces secondary ions from the surface atomic layers which are analysed by mass spectrometry.

The SIMS technique involves bombarding the surface with high-energy ions (known as the "primary" ions) that initiate collision cascades among the surface atoms [Figure 2]. As a result, some atoms and clusters of atoms are ejected from the surface layer. Those acquiring an electronic charge through an ionization process are known as "secondary ions" and are identified by mass spectrometry. Peak intensities can be converted to concentrations with the use of matched standards, so quantitative information is most easily obtainable at low concentrations. SIMS has the highest sensitivity of all the common surface analysis techniques, which means excellent minimum detection levels. The high data signal intensities mean a fast analysis, and this speed advantage is particularly noticeable in imaging mode. The same primary ion beam can also be used for surface erosion, allowing simultaneous etching and analysis.

SIMS offers both elemental analysis with high sensitivity and information about molecular structure, the latter being especially important for organic analysis. The surface can be examined in three dimensions without additional equipment and without resorting to long analysis times. The use of mass spectrometry even means that isotopes can be individually identified, opening up possibilities for isotopic tracing studies. A few examples showing the SIMS technique in action, using data acquired from a MiniSIMS instrument, will emphasise this point.

Electronic devices such as hard disks, display devices, batteries, integrated circuits and passive components all make use of thin films of materials, with thicknesses anywhere within the range of 1nm to 100nm. Light elements and organic species are often involved in determining the electronic properties of such devices. Chemical analysis of surfaces can be used to supplement or even replace time consuming performance or accelerated lifetime testing, but both the materials involved and the need for a surface specific analysis mean that EDX (energy dispersive x-ray analysis) and WDX (wavelength dispersive x-ray analysis) are unable to provide a full analysis. In contrast, SIMS analyses the surface molecular layer, and can image the distribution of individual species in times measured in seconds rather than minutes. The uniformity of coatings can therefore be quickly established.

For example, Figure 3 shows two images of small electronic components, each 3mm x 5mm in size. Figure 3a shows the uneven distribution of sodium at the surface of one finished component. Figure 3b shows another component, examined at an intermediate stage in the production process, where the analysis revealed a 1mm sized area of higher phosphate concentration. Each of the two images was acquired in just 15 seconds.

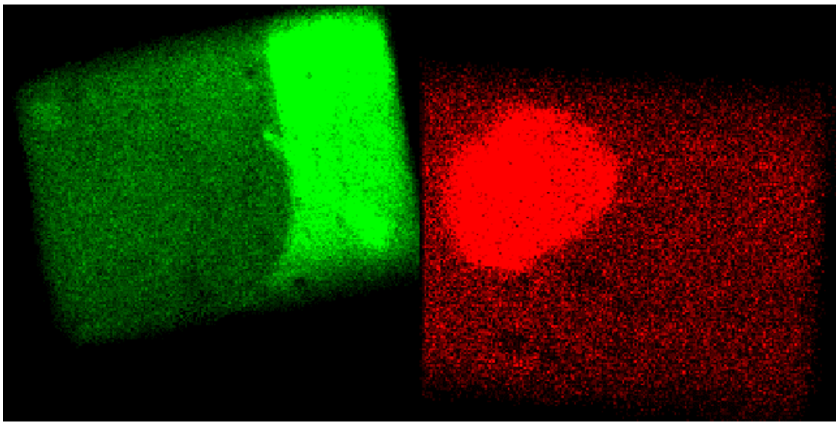

Figure 3 Low magnification SIMS images of two 3mm x 5mm electronic components, showing the surface distribution of sodium (3a) and phosphate (3b). The images were taken at different stages in the production process.

The thickness of a coating is also important in determining its performance. On an atomic scale, the relative intensity of selected spectral peaks that are characteristic of the substrate and coating will reflect the average surface coverage at a sub-micron scale. Once full monolayer surface coverage is exceeded, the spectral peaks characteristic of the substrate will disappear. Depth profiling through the near surface layers then takes over to provide a way to monitor thickness without the need for sample cross sectioning before analysis. Figure 4 shows a profile produced by in-situ etching through a multi-layer coating on a steel substrate. Total analysis time, including loading the sample into the instrument, was less than 30 minutes. The positions of the two interfaces are marked by the rise in the metal oxide signal and the rise in the iron signal as the steel is exposed. The horizontal axis can be converted from etch time in seconds to a depth in nanometres by measuring the physical dimensions of an etch crater. Once this calibration has been performed, the etch time can be used as a routine method of monitoring the thickness of coating materials.

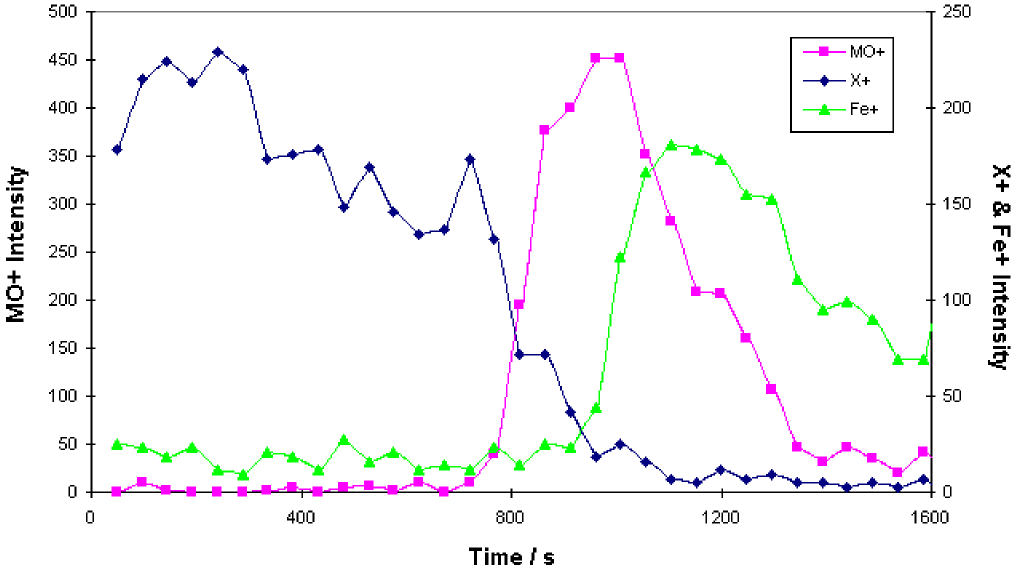

Figure 4 SIMS depth profile through a multi-layer coating on a steel substrate, providing a method to monitor the thickness of the coatings. Etch rate was approximately 0.1nm s^{-1}*. The identity of the ions profiled has been withheld for reasons of customer confidentiality.*

At present, the fastest growing area of surface engineering is in the creation of sophisticated materials for medical applications. Both chemical and mechanical modifications of surfaces are being used to promote growth of a specific type of cell on a surface, or to prevent an adverse reaction such as blood clotting. The example shown here concerns the incorporation of fluorine into the surface of dental materials to provide a persisting protection against subsequent decay. SIMS has a very high sensitivity to the halides and so is an important analysis technique in such work. Initial trials involved preparation of the glass ionomer cement using a fluoride-containing solution instead of pure water, but this resulted in only low levels of fluorine at the surface.

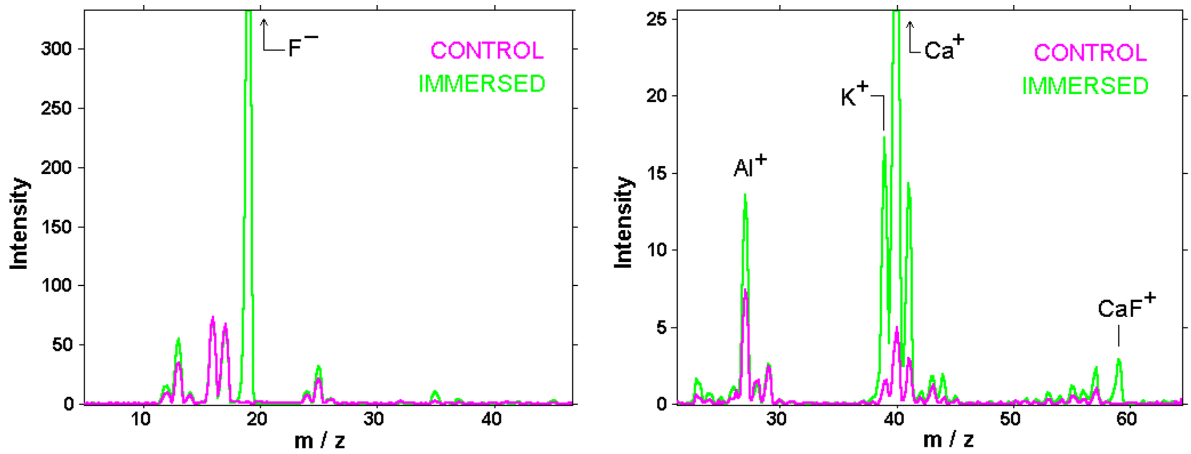

Figure 5 Negative ion (5a) and positive ion (5b) SIMS spectra, demonstrating the surface uptake of fluorine by a dental cement after immersion in a fluoride containing solution. The control sample was immersed in pure water for the same length of time.

Figure 5a demonstrates the successful incorporation of fluorine into the surface by immersion of the cement in a fluoride solution after preparation. Figure 5b provides evidence that this change is associated with elevated calcium levels at the surface. With a data acquisition time of less than 10 seconds for each spectrum, many samples can be screened to help optimise immersion time, solution concentration and other process parameters.

Finally, in the creation of tailored surface properties, any contamination of the surface must be avoided. For example, automotive and aerospace companies are making increasing use of adhesives rather than mechanical fastenings to save weight, and are modifying the surfaces by a pre-treatment before bonding. Nonetheless, the strength and durability of the adhesive joint is still critically dependent on the cleanliness of the surfaces involved. Surface analysis can also help here by identifying the presence of unwanted surface species.

Contaminants such as silicones (siloxanes) cause significant problems even at sub-monolayer coverages as low as a few atomic percent, and so a surface sensitive technique is needed for their detection. Figure 6 shows the surface spectrum of a metal surface covered by polymethylhydrogensiloxane. The presence of the siloxane is revealed by the characteristic peak at $m/z = 73$, but SIMS offers more detailed information. The spectrum is compared to the library spectrum of polydimethylsiloxane (PDMS), and although both share the $m/z = 73$ peak the rest of the spectrum clearly distinguishes the two materials. SIMS therefore offers not just the ability to differentiate between inorganic silicon oxides and organic siloxane, but also allows matching of a contaminant to a specific siloxane. Obviously, the more detailed the information, the easier it is to identify the source of the contamination.

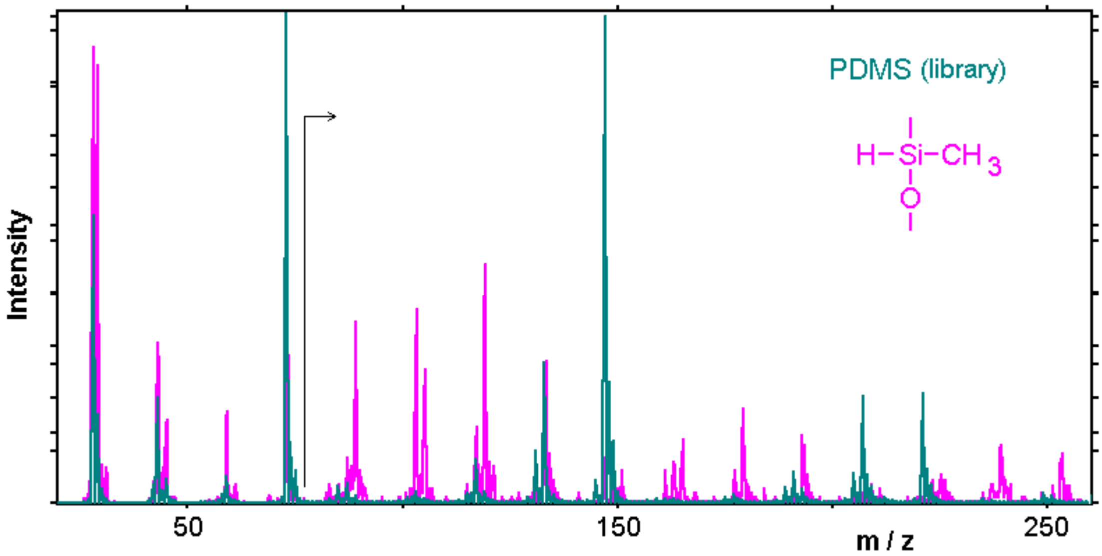

Figure 6 Comparison of the SIMS spectrum from a silicone contaminated surface with a library spectrum of polydimethylsiloxane (PDMS), allowing precise identification of the siloxane involved

There are many more analysis techniques for the investigation of solid surfaces, known by a bewildering array of acronyms. Table 1 (below) compares SIMS with some of these practical surface analysis techniques.

	XPS	**AES**	**SIMS**	**EDX**
Vacuum Required	Yes	Yes	Yes	Yes
Incident Particle/Radiation	photon	electron	ion	electron
Emitted Particle/Radiation	electron	electron	ion	photon
Analysis of Emission	energy	energy	mass	energy [1]
Surface Information	Yes	Yes	Yes	No
Elemental Information	Yes	Yes	Yes	Yes
Molecular Information	Yes	(Yes) [2]	Yes	No
Spatial Information	(Yes) [3]	Yes	Yes	Yes
Depth Information	Yes	Yes [4]	Yes	No
Quantitative Information	Yes	Yes	(Yes) [5]	Yes

[1] or wavelength for WDX [2] limited information can be deduced [3] typically requires long analysis times
[4] requires auxiliary ion beam etching [5] with the use of matched standards

The most widespread technique for the analysis and imaging of solid surfaces is the scanning electron microscope (SEM) fitted with an auxiliary detector to analyse the characteristic X-rays emitted by different elements under electron bombardment. The X-rays are analysed either by their energy (energy dispersive X-ray analysis (EDX or EDS)) or by their wavelength (wavelength dispersive X-ray analysis (WDX)). However, the analysis is typically representative of the surface down to a depth of 1 micron – a huge depth when you consider that surface properties are often determined by the outer atomic layer. In addition, surface engineering is increasingly making use of organic materials, and a simple elemental analysis technique such as EDX/WDX does not provide the information on molecular structure that is required.

X-ray photoelectron spectroscopy (XPS) is a true surface analysis technique. X-ray photons of a specific energy are used to irradiate the surface, causing the emission of electrons with characteristic kinetic energies from the atoms in the surface. Measurement of the energies of these electrons allows calculation of their original binding energy, which identifies the element; the peak intensities provide a quantitative analysis. Shifts in peak position give additional information about the chemical environment of the atom, providing information on surface chemistry. Depth information can be deduced from angle-resolved experiments, or by interleaving XPS analysis with surface erosion by ion beam etching. Spatially resolved analysis is possible, but there is a trade-off in terms of analyzer sensitivity that typically leads to reduced energy resolution or long analysis times.

Another common technique for surface analysis is Auger electron spectroscopy (AES). This is similar to XPS in that it is also based on energy analysis of emitted electrons, but in this case the emission is initiated by a high-energy electron beam incident on the surface. Identification of the elemental composition of the surface is again straightforward, but information about the chemical environment is frequently more difficult, even impossible, to establish. The incident electron beam can be focused and digitally scanned (rastered) over the surface to produce images with high spatial resolution. Depth information can again be obtained by interleaving the analysis with surface erosion by ion beam etching.

These surface analysis techniques are necessary tools to evaluate novel surface layers and relate their functional performance to their chemical composition. The introduction of a desktop instrument, like Millbrook's MiniSIMS, is a cost effective way to address the many situations where the full performance and flexibility of a conventional instrument is not required, but only a true surface analysis technique, like SIMS, will provide the answers.