

Thin Film Characterization using MiniSIMS and ToF-MiniSIMS

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The main advantage of thin films (or any other coating) is that materials properties can be transferred to a surface (thus enabling the use of non specialised substrates). The substrate and the thin film together form a material system which provides the required functionality. There may well be technical reasons (eg electrical capacitance or mechanical considerations) why the films deposited must be thin.

In general however there will also be economic reasons why films should be thin related to the high cost of the deposited material versus the substrate material. Ultimately, monolayer thin films could, in some instances, provide the desired properties. The thickness of the “thin” films mentioned here is considered to be below the order of a few hundred nanometres.

In general, nanotechnology provides the tools for controlling 3 key parameters for thin films performance: chemical composition (and crystalline structure at nano-sized domains), thickness and topology (including nano-scale patterning of a thin film surface) and the most important properties are optical, mechanical and chemical. Of course, in many applications, it is exactly the combination of properties (often the transparency combined with chemical or mechanical properties) that exploits the nanoscale most.

The chemical properties are clearly extremely important. Thin films can be designed to have properties such as water repellence, anti-fogging or provide chemical barriers and chemical inertness, or oxygen or moisture barriers over polymers or antimicrobial surfaces. The functionalisation of polar/apolar surfaces is crucial for sensor applications as may be the degree of hydrophobicity. The appropriate chemical composition (e.g. hybrid coatings) can confer good etch barrier characteristics (e.g. for plastics on automotive bodies) or has a great impact on electrical properties (e.g. in SiOxNy) and especially on insulation properties (relevant for semiconductor circuit structures).

Increasingly polymer thin films are employed and now they make up nearly half of all thin film material production. There are some important reasons behind this fact. Firstly, they are applicable in a huge variety of applications, ranging from organic light emitting displays (OLEDs) through to simple anti-corrosion coatings. Moreover, organic thin films can be applied at low temperature (as compared to ceramic/inorganic materials) and therefore can be handled by less sophisticated processes (e.g. sol-gel).

The main generic bottlenecks identified in thin films research and development are:

1. Lack of understanding of adhesion mechanisms between thin-film/substrates and between different layers.
2. Lack of software for modelling and simulation of thin films formulation and performance resulting in long development time and expensive trial and error approaches.
3. Lack of equipment for meaningful and quick characterization
4. Lack of understanding of industrial environments that require integration into existing production processes.

Considering item 3, the most commonplace micro- and nano- scale materials surface investigation tool has been the SEM / EDX combination. Whilst this combination is still extremely useful, the drive to thinner layers and increasing use of organic materials already alluded to above means that there is often a need for more surface specific analysis and in addition, a technique which can analyse organic molecules in addition to purely elemental species. Whilst surface analysis techniques such as AES, XPS and SIMS have been around for a long time, to date they have required relatively large investments in terms of capital and operating costs.

The advent of the desktop MiniSIMS has reduced the cost of unit sample analysis by an order of magnitude compared with some classic UHV SIMS systems making this technique now a viable in house option especially powerful in combination with the more usual SEM/EDX facilities. The high throughput and ease of use of the MiniSIMS provide the user with a true surface tool equally at home in research and teaching environments as in industrial quality control or failure analysis labs.

The live demonstration of the Millbrook MiniSIMS at the MIICS workshop will demonstrate the power and ease of use of a desktop SIMS in surface (static SIMS), imaging and depth profiling (dynamic SIMS) modes. SIMS works by bombardment of the surface with high energy ions (the primary beam) producing secondary ions from the surface atomic layers of the sample under investigation which are then analysed 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 as a function of depth. SIMS offers both elemental analysis with high sensitivity and information about molecular structure, the latter being especially important for organic analysis.

Recently, a novel Time of Flight version of the MiniSIMS instrument has been developed which has several important advantages over the original quadrupole mass analyser version and also some over conventional ToF-SIMS instruments.

Most ToF-SIMS instruments are designed for maximum efficiency, and use a pulsed incoming primary beam. In fact, the primary beam is typically only active for <1% of the elapsed analysis time. Therefore, although cumulative primary ion dose is minimised, long analysis times are required. The ToF MiniSIMS uses a novel design of analyser and detector where pulsing is instead applied to the secondary ion beam. This allows a continuous primary beam to be used, which maximises data acquisition rates and minimises the time taken to complete the analysis. The more efficient use of the sputtered material described above therefore translates directly into analysis times that can be more than 300 times faster than the quadrupole version of the instrument.

As well as the capability for faster analysis, the ToF spectrometer also means improved analysis in situations where the bombarding primary ion flux must be kept to a minimum. One such case in a typical failure analysis laboratory would be the identification of a small defect or surface contaminant. Sometimes SEM/EDS can give the answer, but often the contaminant is of a nanoscale thickness, and is therefore too thin to provide a meaningful EDX analysis. It is even more frustrating when the contaminant is organic in nature - even when an EDX spectrum can be obtained it does little more than reveal the presence of carbon without any information on molecular structure. What is needed in such cases is a mass spectrometry technique with high surface specificity, which is exactly what SIMS – quadrupole or ToF - has to offer.

The original quadrupole MiniSIMS provided good identification of organic material from large (e.g. 1 mm diameter) contaminated areas. However, in smaller areas (< 0.1 mm diameter) the amount of material available in the surface layer decreases by several orders of magnitude. The limited efficiency of the quadrupole mass spectrometer meant that only part of the mass spectrum could be acquired before the signal started to degrade. This partial spectrum was often sufficient to confirm or exclude a suspected source of contamination, but completely unknown contaminants were not always identifiable.

In such cases the additional power of the ToF spectrometer comes into its own. By analysing secondary ions of all masses simultaneously, a full spectrum can be acquired from these smaller areas before the signal starts to degrade. Typically, complete positive and negative spectra can be acquired in under 30 seconds from an area of just 0.04 mm². The characteristic peaks over the full mass range can be compared with library spectra, and the contaminant identified.

The spectra obtained with the ToF-SIMS spectrometer are notably superior, for instance in looking for higher masses (over 1000 Da). The secondary ions seen at lower masses (100 – 300 Da) represent characteristic fragments of the whole molecule, and therefore provide significant information on molecular structure. However, the peaks observed at higher masses give even more detailed information on organic structure. For many biological molecules and polymer additives, this extended mass range means that a peak corresponding to the complete molecule can be observed, allowing an unambiguous identification.

A further advantage is that the ToF spectrometer can be operated in a high mass resolution mode to separate peaks at the same nominal integer mass. This is particularly useful to differentiate between elemental and organic species, for example to identify aluminium (Al^+) in the presence of surface hydrocarbons (C_2H_3^+). Although both these ions have a nominal mass of 27 Da, at higher mass resolution the peak can be split into the two component peaks at 26.982 and 27.024 respectively. This again reduces ambiguity in data interpretation.

Unexpectedly, all this additional capability is actually gained with a reduction in complexity for the user! This is because the simultaneous detection of all secondary ions means that the operator does not have to make choices during the analysis about which secondary ions to monitor or in what order. Instead, one complete data set can be acquired from a single sample run, consisting of a set of pixel co-ordinates in 2 or 3 dimensions (depending on whether just imaging or a depth profiling experiment is performed) and a full mass spectrum associated with each pixel. The data “cube” (actually a multidimensional array) can then be analysed later using one of many “views” without further data acquisition.