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Extreme Microscopy - at the Surface

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There is much discussion these days of Extreme Sports – sports that push the individual to the limits of his or her capabilities. The title of Extreme Microscopy might conjure up similar visions of intrepid and adventurous analysts, but this article is more concerned with situations that push the technique rather than the operator to the limits. “Extreme” in this context also refers to the information depth of the analysis technique. The properties of many modern materials, particularly those developed by the electronics and biomedical industries, depend on their surface chemistry. This will have been carefully engineered, utilising layers of nanometre thicknesses. These materials demand analysis methods that limit information to the extreme or outermost surface, and eliminate unwanted interference from the bulk or substrate. For current and future generations of such materials, only extreme microscopy will do.

“A picture is worth a thousand words” might be an over-used cliché, but all forms of microscopy demonstrate the truth of this expression. An image can communicate key information more rapidly and effectively than words, tables of figures or even graphs. As a result, many forms of microscopy have developed for imaging the appearance of materials. These range from a simple low-magnification optical inspection microscope to high-resolution instruments that can produce images on an atomic scale such as the Atomic Force Microscope (AFM). Such topographical images are often impressive, but they may contain little or no information about the composition of the material. To overcome this limitation, imaging versions of many chemical analysis techniques have been developed, giving the capability to reveal a chemical rather than a physical image of the surface of a material.

The Energy (or Wavelength) Dispersive X-ray analyser (EDX or WDX) fitted to a Scanning Electron Microscope is one of the most commonly encountered forms of chemical imaging. This is a versatile and powerful technique, albeit one with some limitations. These weaknesses include poor sensitivity to light elements and no information about the structure of organic molecules. However, for the extreme microscopist, the EDX/WDX technique has a much more major drawback – it simply does not produce an analysis of the true surface. The probing beam of electrons penetrates a significant depth into the sample, and the escape depth of the characteristic X-rays that contain the chemical information is also large (Figure 1a). As a result, an EDX or WDX analysis will typically represent not the outermost surface but rather the average material composition over a depth of 1 micron. Reducing the energy of the incident beam reduces the distance that electrons penetrate beneath the surface, but also means the energy is too low to produce the main transitions. The analysis depth cannot therefore be reduced without also producing a rapid decrease in effective sensitivity, and a practical lower limit might be considered to be of the order of 100 nm. This is still far too deep for extreme microscopy.

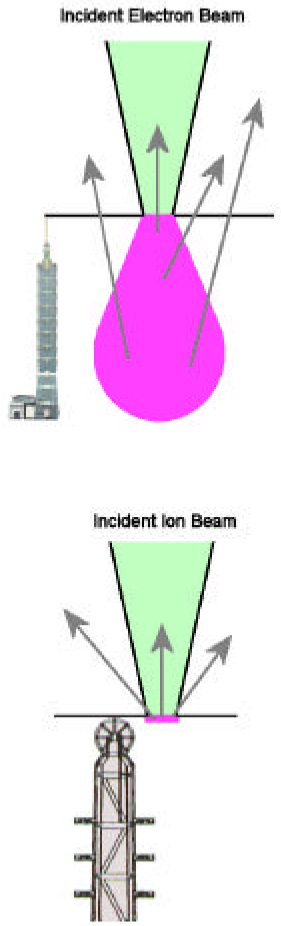
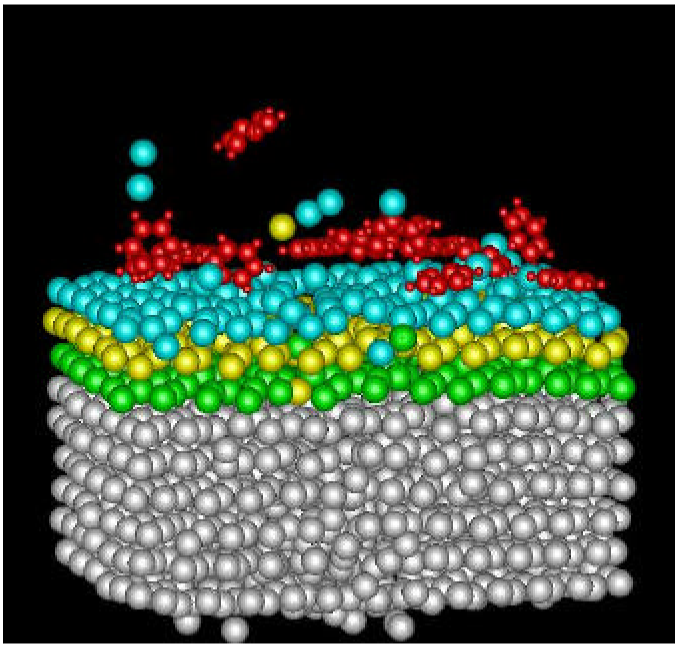


Figure 1 The relative information depths of (a) EDX (1 µm) and (b) SIMS (1 nm). Also shown for comparison is the world’s tallest building Taipei 101 (508 m) on the same relative vertical scales.

So how do we obtain the informative power of an image in combination with the surface specificity required for advanced materials? Fortunately the three most common extreme surface analysis techniques of Secondary Ion Mass Spectrometry (SIMS) (Figure 1(b) and Figure 2), X-ray Photoelectron Spectroscopy (XPS / ESCA) and Auger Electron Spectroscopy (AES / SAM) all have the capability to produce an image of the surface. This can be done in two distinct ways. The microscope approach uses a defocused stationary probe beam and an analyser that retains the spatial relationship of the emitted particles. However, this places restrictions on the achievable transmission of the analyser, and these effects become more severe as spatial resolution is improved. To achieve higher magnification, it is usually more efficient to use a microprobe design. This means that the incident beam is focused and moved over the surface to build up the image one point at a time. This is an inherently slower procedure, but high quality images can still be obtained in analysis times of between a few seconds and a few minutes.

Figure 2 The SIMS sputtering process showing that secondary ions originate only from the near surface atomic layers. The image is one frame taken from a computer-generated simulation (courtesy of Dr Zbigniew Postawa, Jagiellonian University, Poland.



The last five years have seen great advances in the imaging capability of all three techniques. Although the Nano- prefix is perhaps over optimistic, there are now commercially available instruments with trade names of the NanoESCA (150 nm spatial resolution), the NanoSIMS (50 nm spatial resolution) and the NanoSAM (3 nm spatial resolution). However, the state of the art performance embodied in these instruments is achieved only by intricate, high precision design. This results in systems that are very expensive to buy, expensive to maintain and complex to operate. A different approach to instrument design is to aim for an instrument that satisfies the key requirement of extreme surface imaging, but in a form that is inexpensive and easy to use rather than having the ultimate performance specification. Just one of these three techniques, SIMS, exists as a low-cost, user-friendly desktop instrument, and that instrument is the Millbrook MiniSIMS.

The MiniSIMS (Figure 3) is a compact desktop instrument, designed for fast, automated analysis. Preparing and inserting a sample for analysis typically takes just a few minutes. The majority of analyser parameters are pre-set, so there is minimal set-up time and no requirement for repeated calibration of the instrument. The instrument is also designed for high reliability, and can even be moved between different locations. The analyst controls the instrument via a Windows™-based PC, and the basics of operation can be learnt in just a few hours tuition. The actual analysis takes advantage of the high signal-to-noise ratio of SIMS, which means high sensitivity and fast data acquisition times. For example, the individual images shown here were each acquired in about 5 minutes, although imaging times as short as 15 seconds are often used. As well as images, the MiniSIMS can generate mass spectra with an information depth of around one nanometre, sufficiently extreme for even the most demanding surface analyst. For multi-layer materials, the instrument can also be operated in depth profiling mode, where the surface is progressively etched away to reveal the sub-surface layers for sequential analysis.

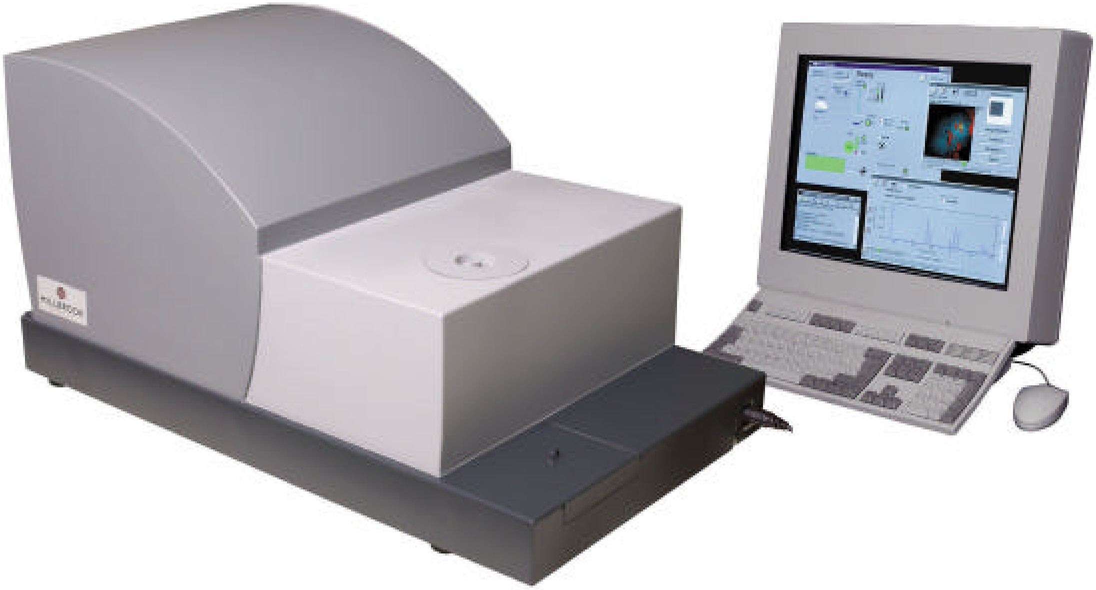


Figure 3 The Millbrook MiniSIMS, a cost-effective desktop instrument, but nonetheless one capable of extreme surface imaging. Further details can be found at www.millbrook-instruments.com.

The recent emergence of this type of cost-effective instrumentation means that extreme surface microscopy can now be utilised in industrial settings rather than being confined to a university laboratory. Applications for the MiniSIMS include monitoring of product quality and failure analysis. As an example, Figure 4 shows part of the connection frame for a semiconductor integrated circuit. The connection points at the end of the “fingers” should be uniformly coated with a precious metal overlayer to allow a high strength, high conductivity bond to be made with the connecting wires. The MiniSIMS images clearly show that on some of the connection points this coating has a patchy distribution. This fault can either result in a failure to make the connection at all, or more seriously produces a low strength bond that subsequently leads to product failure in the field. As the size of electronic devices decrease, the area available for each connection is also decreasing, and it is becoming even more important that the full area contributes to making the bond.

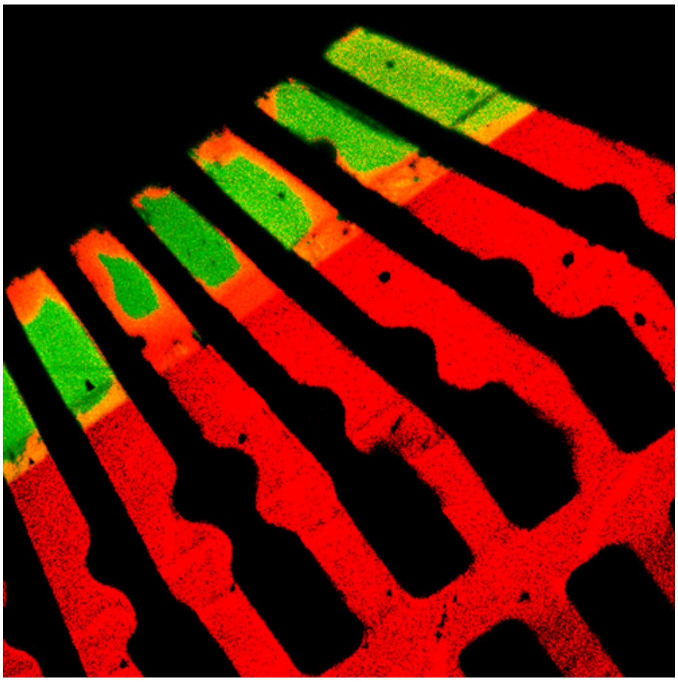


Figure 4 A false colour image, showing part of a semiconductor connection frame. The copper frame is shown in red (Cu+) and the patchy distribution of the thin metal overlayer (M+) on the contacts is shown in green. Image size 3 mm x 3 mm, total acquisition time < 10 minutes.

Other than examining coatings of nanoscale thickness, one of the most common reasons for requiring an extreme surface image is to detect and identify surface contamination. Small particulate contamination can often be successfully analysed by EDX, but drying stains and organic residues are more typically present as a thin film covering a relatively large area. In the extreme, the layer may be only a molecular layer thick. Once again the surface specificity of the MiniSIMS is required, and the mass spectrometry basis of SIMS means it is well suited to the analysis of organic contaminants. The most intense fragment ions can then be used for fast mapping of the distribution of the contaminant. For example, Figure 5 shows part of a biomedical device, a screw intended for implantation into bone; cleanliness is obviously vital to ensure the screw performs as intended. The MiniSIMS analysis identified the presence of both organic and inorganic surface residues, which were then imaged using the CN^- and Cl^- secondary ions respectively.

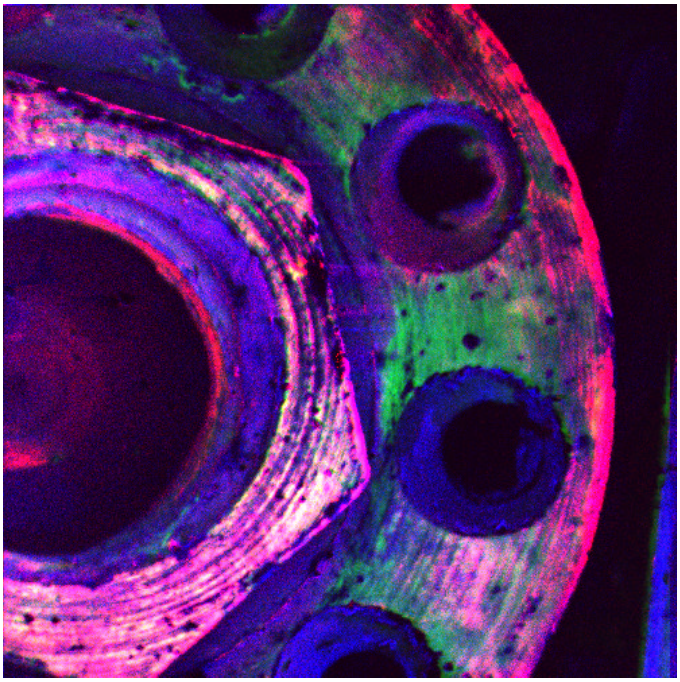


Figure 5 A false-colour image showing part of a bone implantation screw in blue (O-). The location of organic contamination is shown in red (CN-) and the location of inorganic contamination in green (Cl-). Image size 2.5 mm x 2.5 mm, total acquisition time < 15 minutes.

In conclusion, instrumentation now exists to allow chemical images of the extreme surface of materials to be acquired with an information depth as low as one nanometre. As well as recent advances in achievable lateral resolution, low-cost instrumentation has also been developed for routine analysis in an industrial setting. This type of compact instrument is even sufficiently mobile and robust to be taken to remote and hostile environments, allowing an on-site analysis for immediate results. Extreme Microscopy in Extreme Locations – now there's a thought for the future.

Further Reading

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

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