

Recent developments in nano-characterization of materials

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There have been many remarkable developments in characterization techniques in recent years. The relevance of some of the most important advances for nano-materials is discussed in this paper. Thus scanning electron microscopy (SEM) has a backscattered diffraction capability as well as improving (e.g. 1 nm) resolution. Focussed Ion Beam (FIB) instruments provide in-situ etching and deposition capability as well as ion and electron imaging. Transmission Electron Microscopy (TEM) is approaching 0.1 nm image resolution, and 0.5-1.0 nm chemical mapping through energy-filtered imaging. Surface analysis techniques can also now provide elemental distributions at ever improving scales: about 10 nm resolution for Auger Electron Spectroscopy (AES), 50 nm resolution for Secondary Ion Mass Spectrometry (SIMS) and 5-10 μm imaging for micro-X-ray Photoelectron Spectroscopy (XPS). Other techniques such as X-ray diffraction, optical and scanning probe microscopy would normally also be included in such a comprehensive, modern materials characterization facility.

Key words: Characterization, electron microscopy, focussed ion beam, surface analysis, nano-materials.

Introduction

The burgeoning field of nanotechnology promises many developments of new materials and devices. These often require novel fabrication methods, which might embrace chemical or physical vapor deposition, solution chemistry, biochemical or biological processes, or a combination thereof. Naturally the structures to be attained are on the "nano" scale, so their structural determination presents interesting challenges. In fact, the feed-back loop (e.g. Fig. 1) from nanofabrication-to-nanocharacterization is an essential component in refining and making efficient the development process. Accordingly, the characterization techniques play an increasingly important role. Moreover, the instruments responsible are becoming more and more sophisticated, and unless a researcher has been closely following their improvement, the capabilities available now and in the near future may appear to be astounding! This article briefly reviews the most common methodologies which would typically be available in a well-equipped materials characterization laboratory.

Characterization Techniques

Some of the most important pieces of information required about nanomaterials concern their shape, size and distribution, their crystal structure and imperfections, their chemistry and homogeneity, and because of the

large surface-to-volume ratio, the nature of the surfaces themselves. No single technique can provide all these data, so a combination of approaches is obvious. Microscopy yields the overall visual perspective, surface analysis the external chemistry. Examples of these approaches are now discussed.

Scanning Electron Microscopy (SEM)

With the scale and three-dimensionality of nano-materials, the resolution and depth of field of the SEM makes it the most appropriate technique to initially characterize their appearance. Optical microscopy, being limited by the wavelength of visible light, is becoming less useful in this field. Using a short focal length objective lens combined with a high brightness, field-emission gun source, about 1 nm resolution is achievable in favorable circumstances. This does not of course allow visualization of detail at the atomic level, but can address countless problems involving sample structures.

Previous drawbacks associated with SEM concerned the difficulty of obtaining crystallographic and chemical information on a localized scale. The former is now

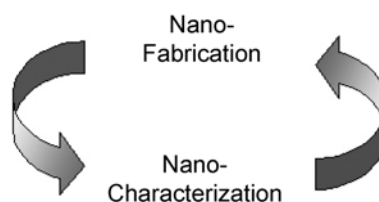


Fig. 1. A feed-back loop from nano-fabrication to nano-characterization is becoming essential for developments in nano-technology.

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overcome by the backscattered electron diffraction capability which is a straightforward accessory on modern machines. Likewise, reducing the beam spreading in bulk samples for X-ray microanalysis is achieved by low-voltage SEM, although the majority of the X-ray signal emanates from below the surface, which is often not portrayed in the image. Low voltage operation (e.g. 1 kV) itself offers some advantages over traditionally higher beam energies [1], and the ease of switching from one to the other is facilitated by computer-stored pre-set alignments.

Focussed Ion Beam (FIB) Microscopy

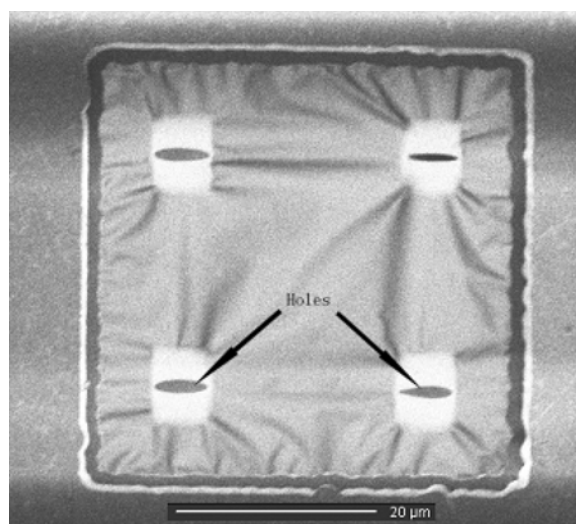
A dual beam FIB allows examination of a bulk sample using either a scanning focussed ion beam (typically Ga^+) or a scanning electron beam as in the SEM, both concentrated at the same position on the specimen. The ion-beam image, employing the secondary electrons created by the impact, is not as clear as the SEM image (currently about 7 nm resolution versus 3 nm or better for the electron image) but can have some advantages when crystallographic contrast in fine-grained materials is sought. However the ion beam itself can be employed in several useful ways. Firstly, it can be used to etch away a surface, thus allowing examination of the component or device section by section. This is particularly advantageous for cross-sectioning through integrated circuit structures. Secondly, the etching can be controlled to create two parallel trenches into a site-specific region in the sample, with a thin sliver remaining. The latter can then be removed and attached to a standard grid for subsequent high-resolution transmission electron microscopy (TEM) examination. Alternatively, thin areas can be etched into the material itself, which are then amenable to transmission SEM observation in the same



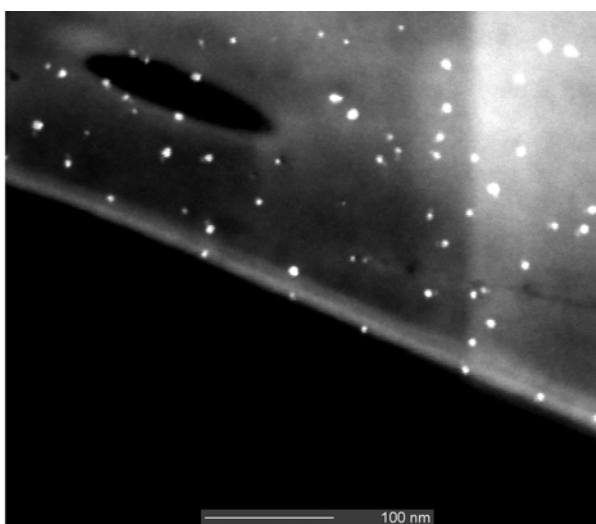
Fig. 2. Metal (Pt) deposition and ion-etching into a Pt substrate.

machine. Furthermore, complex shapes can be fashioned, using the etching capability, for various types of physical testing. Finally, the interaction of the ion-beam (or sometimes even the electron beam) with an organo-metallic gas fed into the chamber can be used to deposit metal or other materials, as dots or lines, which can act as local electrical contacts in very confined areas for instance (e.g. Fig. 2).

An example showing the etching of wedge-shaped holes into silica is given in Fig. 3a. Deposition of small iron particles onto this substrate is revealed by the dark-field scanning transmission electron image (Fig. 3b) and subsequent growth of carbon nanotubes from these particles is nicely illustrated by the secondary electron SEM image (Fig. 4).



(A)



(B)

Fig. 3. (a) Wedge-shaped holes are etched by the FIB into a silica substrate, which provides thin electron transparent areas for TEM. (b) Transmission SEM pictures of iron nano-particles (bright) deposited onto the above substrate.

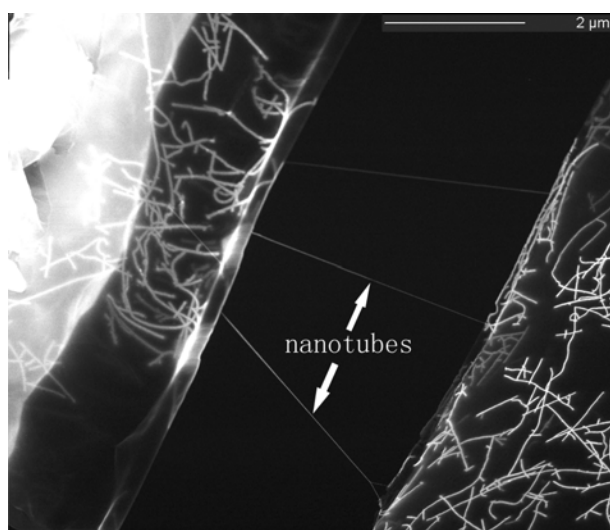


Fig. 4. SEM images of carbon nanotubes grown on the substrate shown in Fig. 3.

Transmission Electron Microscopy (TEM)

When direct imaging of the atomic structure and the distribution of crystal imperfections is required, then the TEM must be employed. As 0.2 nm resolution is merely routine nowadays, and atomic diameters are typically 0.25 nm, atomic resolution is readily achieved. Some specialist instruments involving high accelerating voltages (e.g. 1 MV) or image restoration can bring about 0.1 nm resolution, but the most recent development involves the long-awaited introduction of spherical aberration correction [2] and superior beam monochromatization. Accordingly, one can expect 0.1 nm images to become commonly accessible and even electron probes of this dimension which can either be scanned (to create a STEM image) or focused for purposes of microanalysis.

In addition to this increase in imaging power, the most significant recent improvement has come from the use of characteristic energy loss electrons to create “energy filtered images”. These provide chemical maps of elemental distributions which can be made quantitative at a resolution of 0.5-1 nm (e.g. [3]). When we consider that X-ray mapping in an SEM or microprobe is typically at the 1 μm level, and the best achieved by scanning Auger systems (see below) is about 10 nm, it is clear that this is a remarkable advance. An example, showing chromium segregation to the grain boundaries in a cobalt alloy magnetic thin film employed in longitudinal recording media for computer hard discs, is given in Fig. 5.

The combination of direct atomic imaging, elemental chemical mapping and the electron diffraction capability of TEM makes it an extremely powerful characterization tool. Computer-assisted alignments and the forthcoming aberration correctors make this type of microscopy more readily accessible for non-expert users, and the application of the FIB for preparing electron transparent

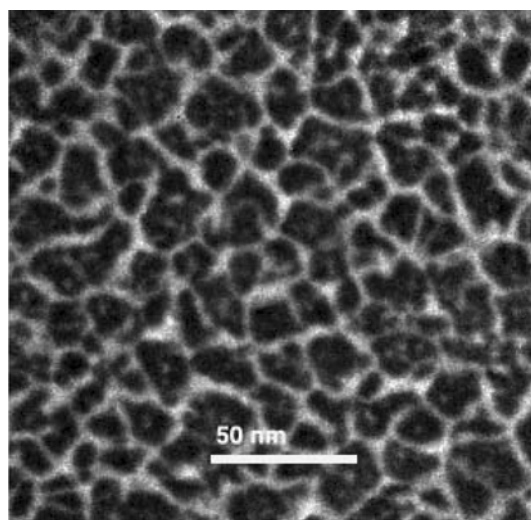


Fig. 5. Energy filtered TEM image showing chromium segregation (bright) to cobalt grain boundaries in a Co-Cr-X-Y alloy thin film used for magnetic recording.

areas for TEM analysis takes away the tedium and difficulty of sample preparation.

Surface Analysis Techniques

There are several surface analytical tools which have somewhat overlapping but distinctly complementary capabilities. As many nanomaterials are grown from a substrate, its surface state is critical to the success or otherwise of the growth process. Figure 6 and 7 show the typical analytical volumes and sensitivity for the most commonly employed methods, AES (Auger Electron Spectroscopy), XPS (X-ray Photoelectron Spectroscopy), SIMS (Secondary Ion Mass Spectrometry) and RBS (Rutherford Backscattering Spectroscopy). As the latter involves a rather high energy ion accelerator, it is the first three which are most appropriate for the modern nanocharacterization facility.

AES employs the elemental characteristic Auger electrons to identify and quantify the elements within

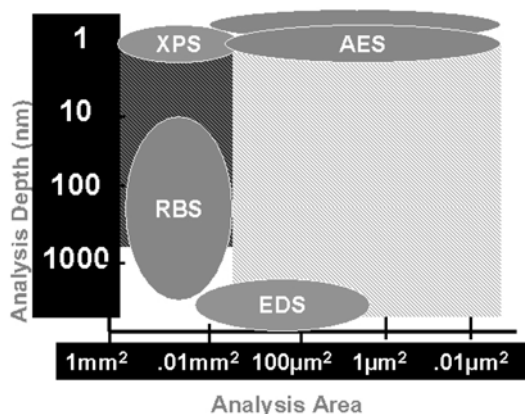


Fig. 6. Schematic diagram showing the depth and analysis range of common surface techniques, including Energy Dispersive Spectroscopy (EDS) in a SEM.

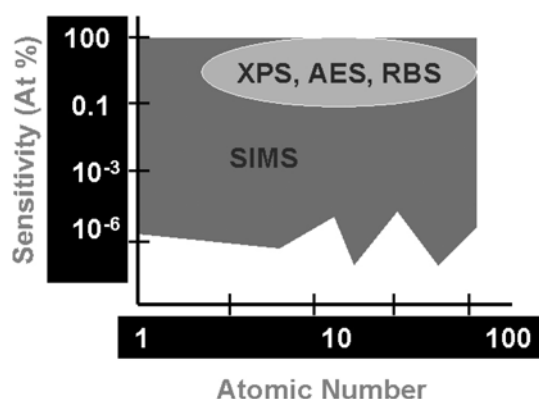


Fig. 7. Approximate sensitivities for the common surface analytical techniques as a function of atomic number.

the top 1-2 nm of a material. As a broad-beam technique, it has gained immense utility when combined with ion-sputter profiling, especially for structures which are layered as in the semiconductor industry. Alternatively, the electron signal emitted from the probed area can be separated into the characteristic energies to yield a chemical map in the SEM mode. These pictures, currently about 10 nm resolution, are much superior to X-ray mapping in an SEM, but are not at the level of energy filtered TEM. However, as they are surface specific, the information can well be different from the latter technique. An example is given in Fig. 8.

XPS bathes the sample with an incident low energy X-ray beam (e.g. Al or Mg K_{α} X-rays), collects and counts the emitted “photoelectrons” which are also only able to escape from the top few atomic layers. Its significant strength arise from the ability to distinguish

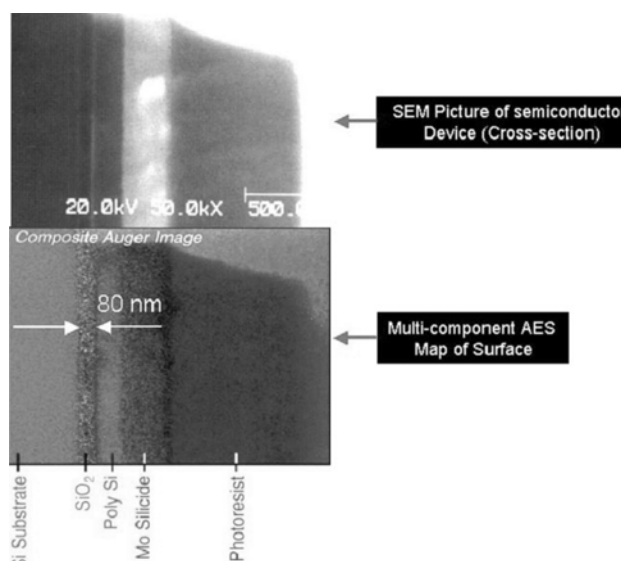


Fig. 8. SEM cross-section image of a semiconductor device structure, and a composite chemical map taken using Scanning Auger Microscopy (Courtesy of PHI/Ulvac company).

photoelectrons with high energy resolution and so identify the ionization state of the elements studied (e.g. Si^{4+} versus Si). Also traditionally a broad-beam technique, by scanning the sample, lateral resolutions on the order of 5-10 μm are achievable, and elements which may not be amenable to X-ray microanalysis in a microprobe are accessible. Micro-XPS, which utilizes a pair of elliptically bent mirrors to focus X-rays from a monochromator exit aperture to a spot size of about 1 μm^2 , thus gives spatial resolution at this level although 10 μm resolution is more typical. An example of a

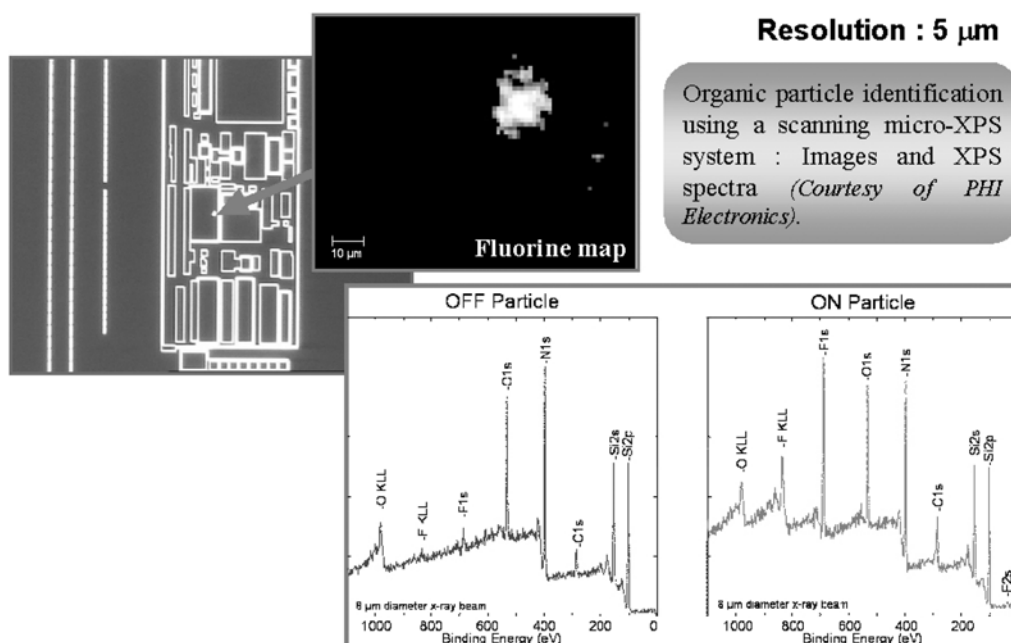


Fig. 9. Micro-XPS imaging of a fluorocarbon residue on a semiconductor chip. Left is an optical microscope image, and the XPS spectra are from on and off the particle (Courtesy of PHI/ Ulvac).

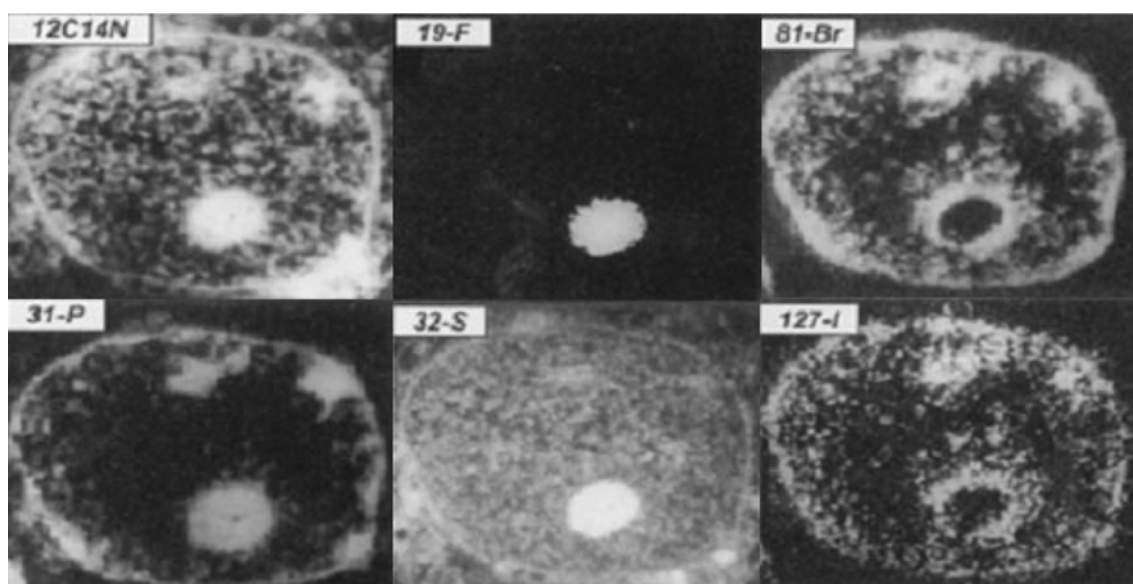


Fig. 10. Nano-SIMS image of various elements in a carcinoma cell (Courtesy of Cameca Corp).

micro-XPS map is given in Fig. 9.

In SIMS analysis, the secondary ions which are created upon bombardment by the primary incident ion beam (Cs^+ or O^-) are identified by a mass spectrometer type system. This is the only technique discussed here which can routinely analyze hydrogen. However, again, through improvements in ion probe formation and detection systems, the analyzed area has been inexorably decreasing and currently is reaching the 50 nm scale level, with further improvements down to 20-30 nm anticipated shortly. Elemental and even isotope analysis is possible and of course mapping using a scanning system. An example is shown in Fig. 10. Of interest is that these levels are sub-cellular, so many applications in biology as well as materials science are expected.

One final point to note here is that although significant advances have been made in these techniques, quantitation without good “standards” is still problematic and is not as sophisticated as, say, a standard electron microprobe analysis. This is especially the case for SIMS, in which the ion yield is very highly element specific.

Complementary Techniques

There are so many methods of “characterizing” materials that the above-mentioned methods certainly need not define a nano-characterization laboratory although there is little question that they would provide a solid foundation. X-ray diffraction, optical microscopy and microprobe analysis are such standard approaches that they are accepted as essential and are often generally available anyway (especially as their cost may not be as prohibitive as the present techniques!). Scanning probe microscopy, and notably atomic force microscopy

(AFM), provides remarkable topographic details which are not even possible in a SEM and distinctly covers the nano-materials size range (generally accepted to be 1-100 nm). Likewise, Raman and Kerr microscopy, and laser ablation can yield information which are difficult to access otherwise. However, the intent here is not to be exhaustive, but rather to give some ideas for a working nucleus for a modern “nanocharacterization” facility.

Acknowledgements

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References and Notes

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4. Techniques and instruments discussed in this paper can be found from the following links:
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<http://www.jeol.com/products.html>
[http://www.hitachihta.com/\(12btp245khh1et45kekt4kre\)/pagelader.aspx?type=product_finder&sttype=technology&text=Electron%20Microscopes&id=5](http://www.hitachihta.com/(12btp245khh1et45kekt4kre)/pagelader.aspx?type=product_finder&sttype=technology&text=Electron%20Microscopes&id=5)
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