

# Analytical Methods for Nanotechnology

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## ABSTRACT

Growth in the micro- and nano- engineering industry has led to increased demand for analytical and characterization methods for these materials and systems. For example, nano-products with high surface area-to-volume ratios are more sensitive to impurities and microcontamination during processing than larger geometry products, resulting in defects and yield loss in production.

New manufacturing methods, materials and processes generally have the same concerns that previously existed for advanced technologies (e.g. cleanliness, contamination, yield, reliability, etc.)

This paper demonstrates contributions that surface analytical methods can make towards problem solving during the manufacture and reliability characterization of new materials. These techniques include: SEM, TEM, XPS TOF-SIMS, Auger electron spectroscopy and XRD. Examples of these techniques as characterization tools in the nano-dimension will be given, with a discussion of their relative strengths and weaknesses

**Keywords:** surface, analysis, contamination, characterization, composition

## 1 INTRODUCTION

### 1.1 Background

Materials characterization at increasingly small dimensions is a critical part of many manufacturing industries, including semiconductors, optoelectronics, automotive and aerospace. All of these industries are increasingly using small scales and more tightly controlled processes as part of the traditional evolution of manufacturing towards smaller, lighter, faster or stronger characteristics, depending on the application. On top of the evolutionary aspect of dimensional shrinkage is the use of 'new' materials or 'new' processes that may carry their own novel properties or design issues not previously encountered..

Products from the world of nanotechnology have numerous uses today and of course, even more future applications. For example sun lotions, wrinkle-free fabrics, nanoparticle paint systems, and nano-filler embedded composites are on the market already. Future uses of nanotechnology promise potential benefits through development of more efficient energy technologies and nanotechnology enhanced water purification. On top of this list of expected and potential benefits are concerns due to

nanoparticle exposure in the environment. Another topic of concern is that of nanomaterials characterization to enhance product yield and functional reliability. Emerging technologies are only acceptable to industry when the producer can make the product in high volume without significant waste for a reasonable return, and when consumer confidence in the product provides a suitable market opportunity.

At first glance, traditional analytical and other characterization methods may be thought unable to cope with the apparently sudden shrinkages in dimensions to the nanometer scale, however, this is not actually the case. Many well established materials characterization methods can be applied to nanomaterials, with minimal modification to established analytical procedures. This is often by virtue of the fact that at least one (or possibly more) of the dimensions of the analytical area are already on or near the nanometer scale (or lower). The aim of this paper is to demonstrate the ability of available analytical techniques to contribute successfully to the nanoscale characterization of materials, thus leading to a fundamental understanding of the materials and also their subsequent incorporation into actual products.

Many analytical techniques available today can provide data on nano-engineered materials [1,2]. These techniques are accepted and well established, although their application to new materials may not be widely known. Development of analytical tools specifically for nanotechnology is underway, yet use of a new measurement with a new technology may result in many questions or unexpected variables in contrast to trusted data with considerable historical context. The costs of instrument development are also extremely high in terms of time, people and capital. The use of proven analytical tools that include TEM, SEM, XPS, XRD, Auger and TOF-SIMS to characterize products of nano- and micro- technology are reported here. A full understanding of product behavior and characteristics throughout the manufacturing process and subsequent lifetime of the product is required for both production and safety reasons.

Areas of concern in processing and use of nanomaterials include: Does the received raw material conform to expectations? How does one perform an incoming inspection on these raw materials? How do nanoparticles cross contaminate during processing? What compositions and shapes of nanoparticles are operators exposed to? Does the product perform in the consumer environment? Are nanoparticles emitted due to reliability failures and how

does one quantify what is emitted? How does one analyze deposition of molecular contaminants that can create high surface energy and stiction failures in MEMS devices? Multiple techniques available today can provide valuable and reliable data to address these concerns.

## 1.2 Information depth and analytical area

In all analytical measurements that are focused on small areas or volumes, it is important that the analytical technique is consistent with the area, volume or region of interest. For example, if a low density distribution of nanometer scale particles on a substrate is of interest, is it appropriate to use an analytical tool with a very wide (millimeter or centimeter scale) analytical area (i.e. much larger than the particles)? Similarly, would it be appropriate to use a technique with an information depth on the micron scale (i.e. much larger) than the scale of the particle dimension of interest? Depending on the circumstances, the answer to these questions could be either yes or no. In the first case, if the particle density is sufficiently high, or the particles themselves are sufficiently different to the substrate then the answer may be yes. In contrast, for the second example, if information about the particles themselves is desired, then it may be inappropriate to use a characterization method which probed deeper than the particles, without an understanding of the consequences.

The range of characteristics of interest may be defined as follows in regards to nanodimensional features (particles and/or films):

1. XY dimensions (i.e. lateral size)
2. Size distribution (i.e. range of particles sizes)
3. Z dimension (i.e. thickness)
4. Composition (bulk and/or surface)
5. Surface chemistry or functionality (i.e. differences between the surface and bulk)
6. Crystallinity and crystallite size

Further factors may also be of interest, depending on the application and type of material.

## 2 EXPERIMENTAL

In order to illustrate the various characteristics of common analytical techniques, two sets of analyses were carried out.

(1) A series of commercially available nanomaterials were acquired. These were then subjected to a range of tests to investigate their composition.

(2) A MEMS sample with a monolayer-range thickness anti-stiction fluorocarbon coating that showed excessive stiction was also analyzed.

The following measurements will be discussed and illustrative examples shown:

1. TEM (Transmission Electron Microscopy)
2. XPS (X-ray Photoelectron Spectroscopy)
3. XRD (X-ray Diffraction)
4. AES (Auger Electron Spectroscopy)

## 5. TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry)

### 2.1 Transmission Electron Microscopy

TEM (JEOL 2010, 200kV) was carried out on Al nanoparticles with a nominally spherical shape and an average size of 18nm (size range of 2-50nm). The particles were sonicated in methanol and distributed on a TEM sample grid. Results show that the particles were actually not all spherical and, in fact, a range of shapes were observed. These included rods and joined particles ('dumbbells'), as seen in Figure 1. Further examination of individual particles revealed an amorphous layer around the outside of the particles (Figure 2). Further TEM-EDS analysis showed that the amorphous layer was oxygen-rich, so was most likely an oxide. No other analytical technique would be able to show the difference between the bulk and the surface of the material with this atomic level of detail.

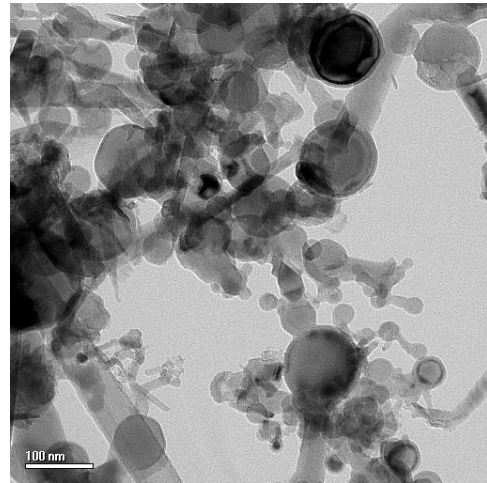


Figure 1. TEM image of Al<sub>2</sub>O<sub>3</sub> nanoparticles (1.5µm × 1.5µm area)

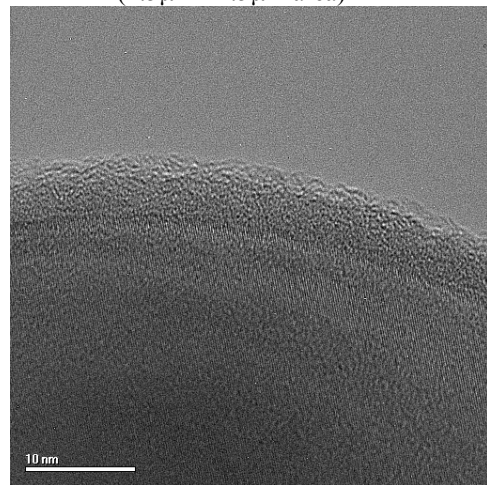


Figure 2. TEM image of Al<sub>2</sub>O<sub>3</sub> nanoparticles (44nm × 44nm area)

### 2.2 X-Ray Photoelectron Spectroscopy

XPS was carried out on several Si and Ti-containing nanoparticles: SiO<sub>2</sub> (30nm), Si<sub>3</sub>N<sub>4</sub> (20nm), SiC (55nm) and TiN (15nm). The information depth of XPS is dependent on both the element of interest and on the angle of incidence of the X-rays, but is typically in the range of 10-100Å. XPS can thus provide information regarding oxidation of particles and alteration of surface chemistry, either through atmospheric exposure or through deliberate processing. Please note that with particles on the nanometer scale, we are essentially doing a bulk analysis of the whole particle and there is no clear distinction between surface and bulk for very small particles. The instrument used was a Physical Electronics Quantum ESCA Microprobe.

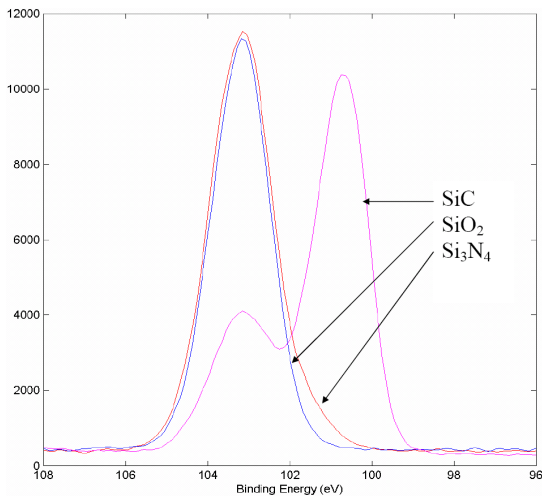


Figure 3. XPS spectra of the Si region of SiC, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> nanoparticles

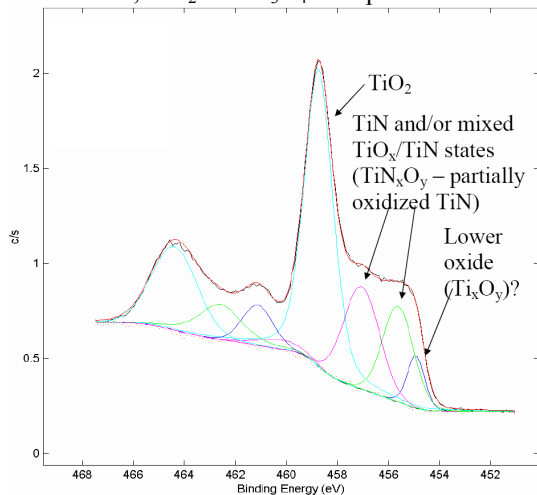


Figure 4. XPS spectrum of the Ti region of TiN nanoparticles, showing mixed oxides and nitrides

Figure 3 shows the Si region of three nanoparticles: SiC, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>. From this spectrum, it can be seen that the SiC particles have significant oxide character and similarly, the nitride particles were also oxidized. Figure 4 shows the Ti spectral region from TiN nanoparticles. It can be seen that this region is complex and that there are multiple oxides and nitrides present. These are tentatively identified

in the spectrum from the peakfits. The relative amounts of these different chemical states can also be quantified, which can be extremely helpful during studies of nanoparticle functionalization and their behavior when exposed to different chemical processes.

### 2.3 X-Ray Diffraction

XRD was carried out on a series of nanoparticles to confirm that their crystalline state matched the expected state of the purchased material. The material detailed in this case was SiC (cubic) with an average particle size of 55nm. Figure 5 shows a 2θ scan obtained using a Panalytical X'pert Diffractometer. The predominant phase was found to be cubic, as expected, with minor contributions from hexagonal and/or rhombohedral phases. The crystallite size of the primary phase was determined to be in the range of 22nm, i.e. substantially smaller than the average particle size of 55nm. This distinction showed that many of the particles consisted of multiple crystallites. As a complement to the wide angle X-ray diffraction discussed above, small angle X-ray scattering can also be done to investigate larger spacings, such as polymer stacking and particle size distributions, which also has relevance to nanoengineered materials.

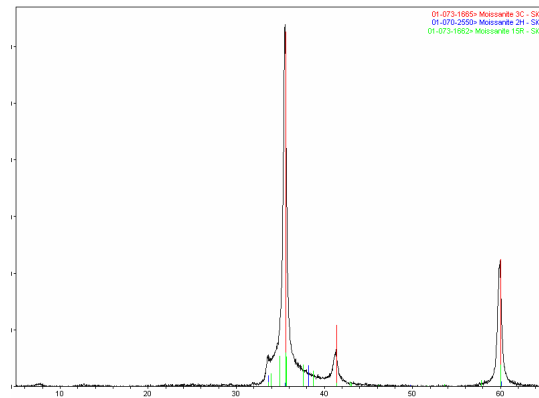


Figure 5. 2θ scan from cubic SiC (55nm size)

### 2.4 Auger Electron Spectroscopy

AES is an excellent complementary technique to SEM (Scanning Electron Microscopy) in that AES can provide elemental maps with significantly better spatial resolution and surface sensitivity than SEM/EDS. The typical information depth for Auger is in the range of 30-60Å, with a spatial resolution in the 10nm range. Figure 6a shows an Auger SEM image obtained from a two-component nanoparticle (Al and Cu) mixture deposited on silicon. Figure 6b shows a copper elemental map and Figure 6c shows an aluminum elemental map, both obtained from the same area as the SEM image. The SEM image and maps were acquired using a Physical Electronics 680 Scanning Auger Microprobe and clearly show the distribution of the separate Al and Cu particles.

Elemental analysis of individual particles showed elemental compositions in the following ranges:

Al: C (43%) Si (20%) Al (19%) O (18%) Cu (0.6%)  
 Cu: C (40%) Si (25%) O (19%) Cu (16%)

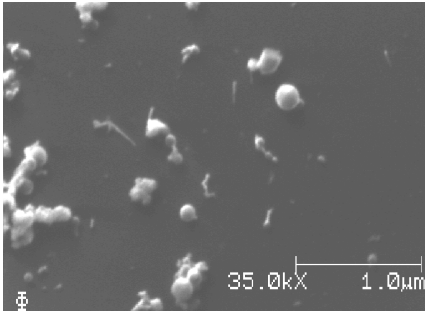


Figure 6a. Auger SEM image of a Cu/Al nanoparticle mix

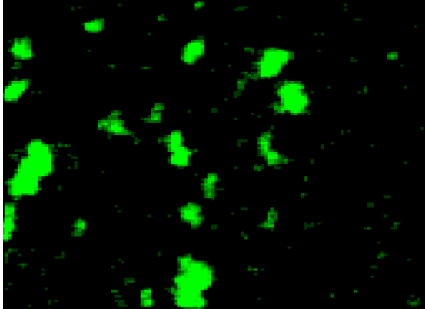


Figure 6b. Copper Auger map

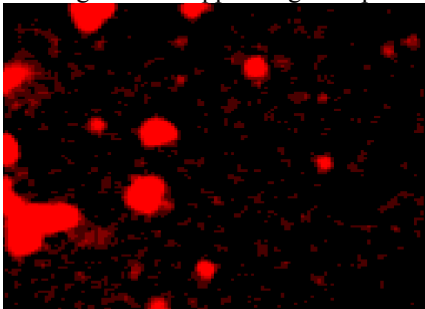


Figure 6c. Aluminum Auger map

The presence of such apparent levels of carbon and silicon is likely to be a consequence of the low information depth of the measurement (for C) and electron scatter from the substrate (for Si).

## 2.5 Time of Flight Secondary Ion Mass Spectrometry

TOF-SIMS does not have the spatial resolution of electron beam techniques such as SEM, TEM or AES, however it has an extremely low information depth, in the range of 10-20Å, meaning that it can successfully provide information from surfaces covered by a monolayers or less of material. This extreme surface sensitivity makes it an ideal technique to examine low levels of molecular contamination on surfaces. This has particular relevance for MEMS devices coated with nanometer thick anti-stiction films such as fluorocarbons, as shown in the following examples. Figure 7a shows data from a contaminated surface that showed poor mechanical response and excessive stiction. Figure 7b shows data from the same

location on a correctly functioning device. The main difference between samples was the presence of various silicon ions on the failing sample. It is suspected that the silicone outgassed from the epoxy sealant used to encapsulate the device and subsequently deposited to the anti-stiction coating surface, inhibiting its effectiveness. The presence of the silicone on the moving structures led to stiction problems during practical operation due to the increase in its surface energy compared to the fluorocarbon coating.

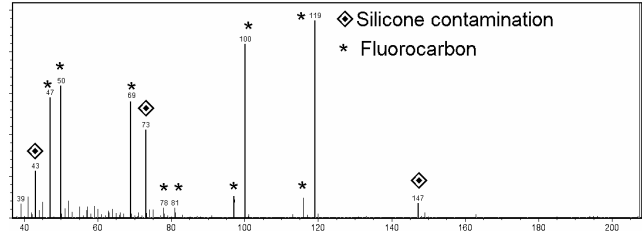


Figure 7a. Contaminated surface

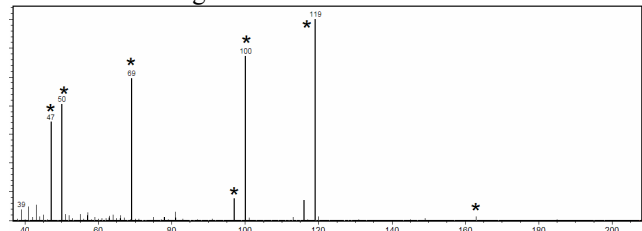


Figure 7b. Clean surface

## 3 CONCLUSIONS

Each of the short cases studies detailed above, and also the discussions of the various analytical techniques have been used to demonstrate some of the capabilities of currently available analytical methods. Further techniques not detailed here can also contribute significantly to nanomaterials characterization. These include Raman spectroscopy, particularly with respect to carbon nanotubes; and AFM (Atomic Force Microscopy), for dimensional and morphology studies. These established techniques can successfully be applied routinely to new materials. Further development and specialization of these techniques is also under way, as is the development and establishment of new analytical methods, to meet the needs of both the nanomaterials community and the needs of all high technology industries.

## ACKNOWLEDGMENTS

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