

Invited, Review

Applying Surface Analysis in Electronics Materials Processing

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Surface chemical analysis by XPS, AES and TOF-SIMS are widely used and recognized as critical for the development and production of electronics materials. Applications in these areas include characterization of microelectronic devices, inorganic thin film structures, organic thin films and even mixed mode devices of organic and inorganic materials. Characterization of electronic materials and processing can be accomplished by assessing as received surfaces, and examining materials by angle-dependent profiling or sputter depth profiling.

1. Introduction

Surface chemical analysis techniques are widely used for the characterization of the materials used in today's modern electronic materials. Surface sensitive methods for analysis, such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) or time-of-flight secondary ion mass spectrometry (TOF SIMS) are often used for process characterization, material characterization and failure analysis. Many of the new materials being used in today's devices present analytical challenges which include spot size or materials that may be beam sensitive.

For manufacturing problems it is often very useful to determine the composition and chemistry of the materials. This information can be used to identify the point in a process where contamination might originate. Likewise baseline characterization of a process can quickly point to a source when a problem arises. Use of surface analytical methods is well-known for determining the chemistry or composition of materials, Brundle [1]. In many cases, it is necessary to use a variety of analytical techniques that include optical microscopy, scanning electron microscopy, transmission electron microscopy, scanning probe microscopy and x-ray diffraction to name a few.

This paper describes the applications of surface chemical analysis to the variety of issues encountered with electronic materials as well as some novel approaches that these complex material systems pose.

2. Experimental

The XPS data were acquired on a PHI Quantum 2000 Scanning ESCA microprobe. The TOF SIMS data were acquired on a PHI TRIFT II system using a gallium ion beam. The Auger data were acquired on a PHI 700 Scanning Auger Microprobe. All of the specimens were analyzed as received without further preparation unless otherwise noted.

3. Results and Discussion

When looking at electronic materials the choice of surface analytical method is often dependent on the question being posed. XPS is often used as the surface analysis method of choice for a first look at a material for characterization or for failure analysis, assuming the area of interest is not smaller than nominally 10 μ m. XPS is relatively benign in terms of sample damage, but is limited in spot size. When presented with an issue of smaller areas TOF SIMS or AES may be better choices. The selection of the method may then depend on whether the area of interest is assumed to be organic or inorganic in nature. Small area organic materials are more suited to analysis by TOF SIMS while small area inorganics are best suited to electron beam Auger spectroscopy.

3.1 TOF SIMS

TOF SIMS is a surface analytical method that samples the first 1.5 nm of a surface. Using a liquid metal ion

gun to direct a low energy beam of ions or ion clusters toward a surface the impinging ions causes the sputtering of material from the surface. Most of the sputtered material leaves the surface as a neutral species. The small amount of sputtered ions can then be mass analyzed with high precision using a time of flight mass spectrometer. This information can be used to identify organic and inorganic materials and contamination.

One example of using TOF SIMS is illustrated in Figure 1 where a residue was noticed on a production wafer both in field regions and in the low level pattern regions. The contamination was too small to be easily analyzed by XPS and the thick non-conductive substrate precluded the use of electron beam Auger spectroscopy. The total ion image of the regions of interest shows the location of the residues. By acquiring a full spectral data set at each pixel of the image it is possible to reconstruct an ion specific image showing the spatial distribution of a particular species. In this case the analysis by TOF SIMS shows that the residues are fluorides which originated

from an etch bath.

3.2 Auger Electron Spectroscopy

Auger electron spectroscopy is a technique where an electron beam is focused on a surface. The interaction of the electron beam with the specimen causes electron vacancies that are filled via a Coulombic rearrangement of the electrons. This relaxation process causes the emission of a photon (used for energy dispersive spectroscopy) or the ejection of an electron with an energy characteristic of the element. Measuring the kinetic energy of the ejected electron provides a means to identify the composition and chemistry of the surface, Strausser [2]. Auger spectroscopy is a surface analysis technique with the highest spatial resolution, down to about 6 nm the surface being analyzed refers to about the first 7 nm of the specimen, similar to XPS. The very high spatial resolution of the AES spectrometer makes this tool invaluable for analysis of electronic thin film materials as well as the particles often observed to create problems in microelectronics.

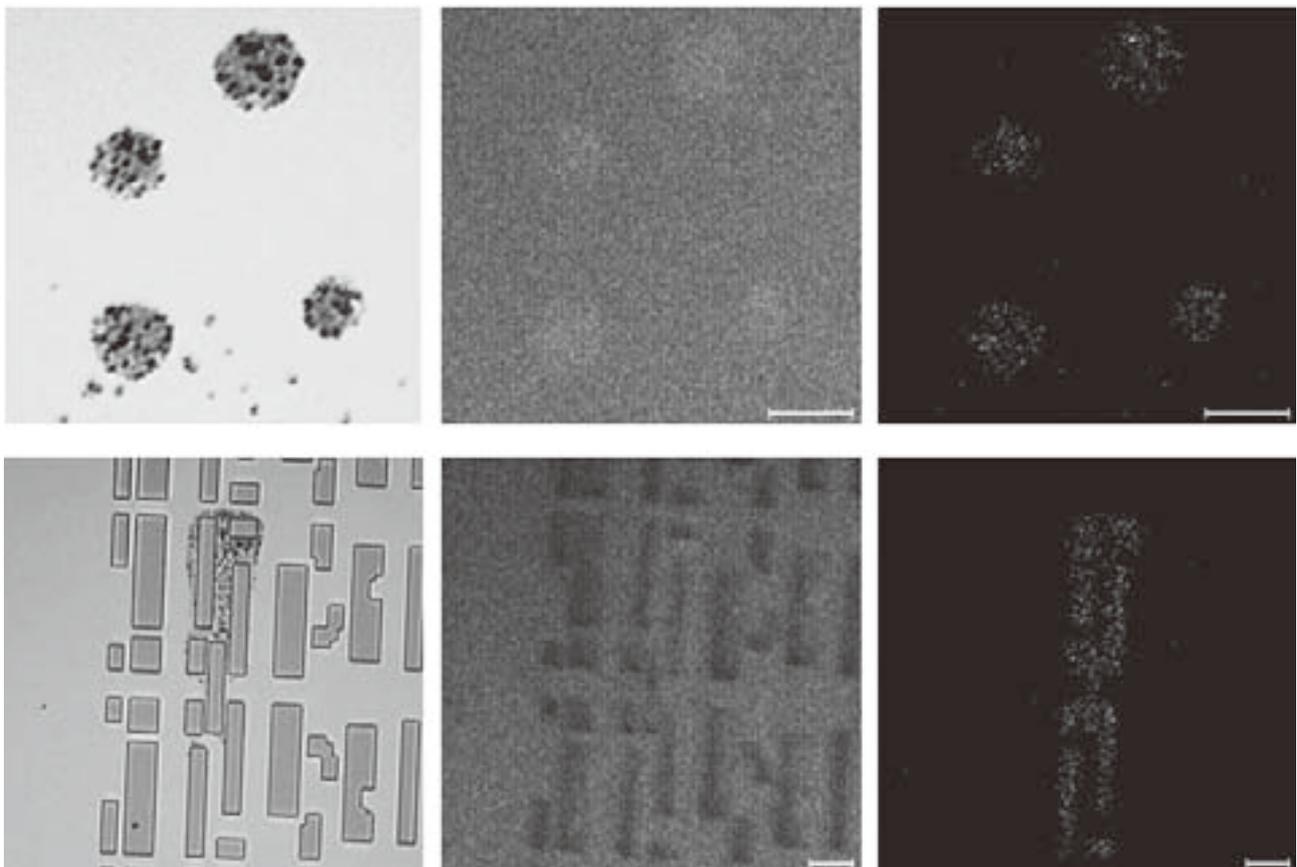


Figure 1 TOF SIMS data of fluoride residues on a wafer surface. Left is an optical image, center is a total ion image and right is a fluoride ion image. The micron bar represents one micron.

In the example illustrated below the sample is a wafer from a multilayer polysilicon deposition. After the deposition the wafer showed a brown stain. The purpose of the analysis was to identify the material causing the brown stain. The secondary electron image taken in the Auger tool shows that the stain is actually a collection of nanowires illustrated in Figure 2. Elemental analysis of the nanowires shows them to be composed of elemental silicon. Auger images obtained from the nanowires shows that only silicon is present and no seed material is observed that would stimulate the growth of the nanowires.

3.3 X-ray Photoelectron Spectroscopy

XPS is a surface analytical technique that samples about 7 nm of the surface of a material based on the photoelectric effect. Soft x-rays impinge on a specimen causing the photoejection of electrons. Determination of the kinetic energy of the electrons identifies the elements present while the intensity of the detected peaks is indicative of the quantity after correcting for the photoe-

lectric cross section. High-resolution spectra can be used to determine the chemical state, or short range chemistry of the observed elements.

XPS is commonly used for the surface analysis of polymers. Surface modification of polymers is applied to enhance the properties of a polymer and XPS is routinely used to monitor changes to the polymer chemistry. A new application in the field of electronics materials is to use organic polymers in organic light emitting diode structures or as the medium for charge transfer in any number of electronic imaging systems. These new applications of organic thin films present significant analytical challenges.

In one case, a mixture of polymers was being used for their charge transfer capabilities, but after a short period of time the material would fail to work correctly. Surface analysis by XPS shows the surface chemistry of both the good and bad material to be identical in chemistry and composition.

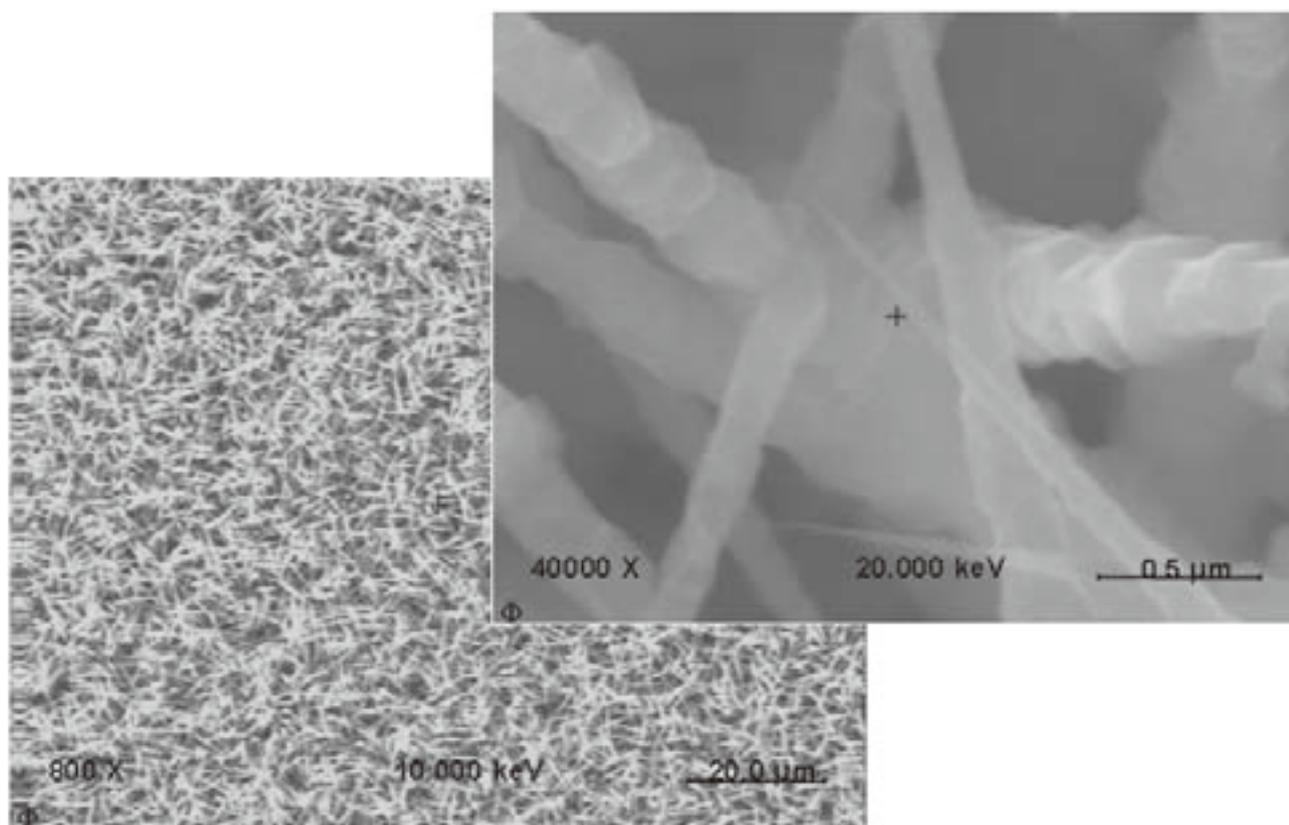


Figure 2 Secondary electron images from the scanning Auger.

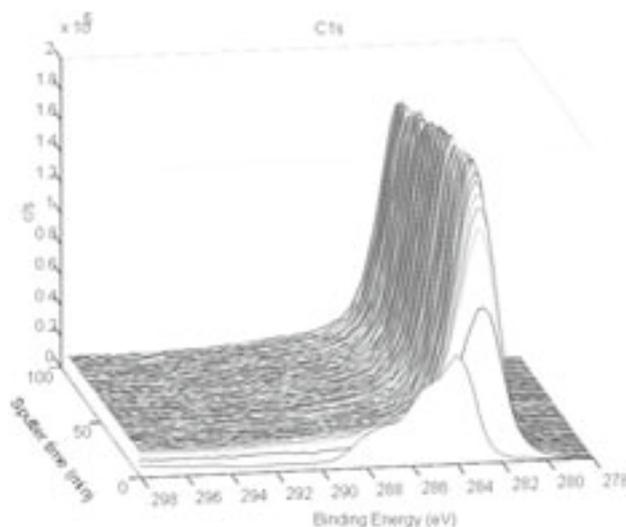


Figure 3 High-resolution carbon spectra from a multi-layer polymer sample

However, due to the nature of how the charge transfer occurs there was a suspicion that the two samples may in fact be different as a function of depth. While sputter depth profiling is commonly used in both XPS and AES for the analysis of inorganic thin films, profiling of polymers is not often used. The reason for limited polymer profiling is that the physical act of ion sputtering typically destroys the chemical information as well as rendering the polymer as amorphous carbon. Figure 3 illustrates the change in carbon chemistry due to ion milling. In this case, the photoelectron peaks showing different carbon chemical environments such as carbonyls and esters are removed leaving a non-descript peak shape characteristic of amorphous carbon. However, if there are hetero-atoms present in the polymer it may be possible to follow these elements and monitor their distribution and use them indicators of different polymer layers. In the case of the two samples of charge transfer material the sputter depth profiles, Figure 4, show that the good sample has a nitrogen depleted layer at the surface and a nitrogen rich layer that is subsurface. New ion gun technology using molecular clusters may be promising for determining the changes in chemistry between these materials. film, is reduced when the titanium electrode is deposited

Another challenging area for XPS analysis is in the investigation of many modern solid-state electronic devices where the critical layers and interfaces are now reaching scales of only a few nanometers thick. These

layers are generally buried underneath thick and complex materials stacks, the fabrication of which frequently alters the chemical and physical properties of the critical interfaces. The conventional approaches for analyzing deeply buried layers employ ion-milling to depth-profile the materials stack down to the critical film or interface. However, such depth-profiling processes often induce chemical and physical changes several nanometers below the exposed surface. This modification of the device stack can reduce the utility of such investigations -- particularly when the critical interfaces are of chemical compositions or physical structures that are easily altered by atom bombardment.

Surface chemical analyses of such materials require novel approaches for investigating the undamaged physical and chemical properties of buried critical layers and interfaces. One approach to this dilemma is to open the interfaces by delamination *in vacuo* and then examine the interfaces by angle dependent XPS. Analysis of

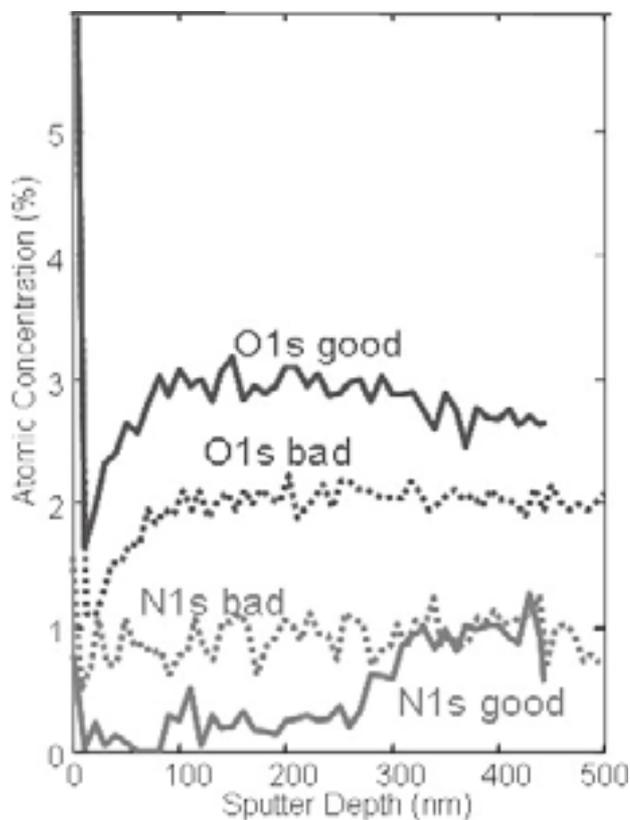


Figure 4 XPS profile data for two polymers. Good (solid) Bad (dotted)

such an interface of a molecular device was performed. The sample was a platinum/ platinum oxide/ Langmuir Blodgett film / titanium/ platinum stack, illustrated in Figure 5. The weak layer in the stack is the LB film and it was expected that the thin film stack would separate there. The sample was delaminated *in vacuo* using a polymer spring mechanism that was activated by the robotic arm of the spectrometer. The subsequent analysis of the substrate and the delaminated lid revealed some surprising chemistry, Donley et al, [3], Blackstock [4]. There was some evidence of the LB film on both the substrate and top (see figure 5 below) after the delamination suggesting that the observed LB film was not continuous on either the top or the substrate. It was also clear that upon deposition of the upper titanium electrode several chemical reactions had occurred. These reactions include the formation of carbides, oxidation of the titanium and the reduction of the platinum oxide layer to metallic platinum. The changes in the platinum chemistry are illustrated in Figure 5 where the thin platinum oxide, covered by a LB leaving no platinum oxide on the substrate. This result was surprising as there is no direct contact between the titanium and the platinum oxide. Angle dependent profiling of the exposed interfaces showed that the titanium layer on the lid was composed of titanium oxides, sub oxides and carbide. The angle dependent data showed that the carbide was near-

est the top of the oxidized titanium film and closest to the top metal platinum and away from the LB film on the substrate platinum. That is to say, when the titanium carbide is formed during the titanium electrode deposition, the carbide ends up being furthest from the LB film once the device is fully fabricated.

4. Conclusions

The common tools of surface analysis, AES, XPS and TOF SIMS, are widely used for the characterization of electronic materials. These techniques are often complementary to other analytical techniques, but their unique surface sensitivity makes them essential for investigating interfacial reactions and contaminations.

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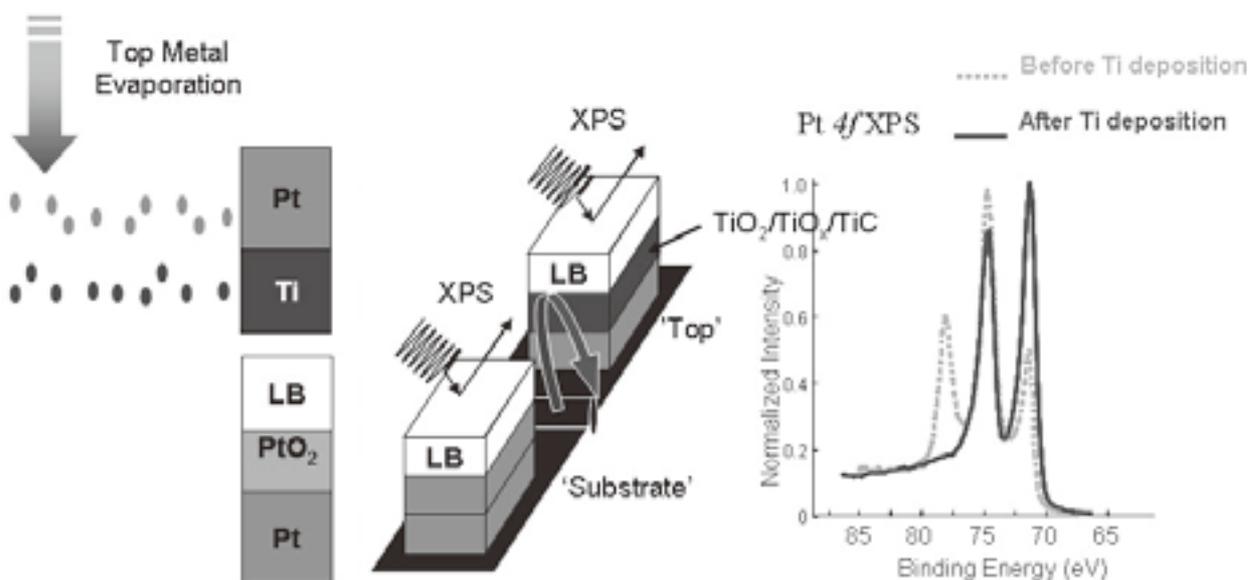


Figure 5 Illustration of the *in vacuo* delamination method. The XPS data of the Pt 4f illustrates the reduction of the platinum oxide during the top metal electrode deposition.

6. References

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