

# Monday Morning, October 15, 2007

## Applied Surface Science

Room: 610 - Session AS-MoM

### Quantitative Surface Analysis I. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

**Moderator:** D. Gaspar, Pacific Northwest National  
Laboratory

8:00am **AS-MoM1 Quantitative Surface Analysis - Applying Thirty  
Years of Progress and Addressing New Analysis Needs, D.R. Baer,**  
Pacific Northwest National Laboratory **INVITED**

Over the past thirty plus years, advances in instrumental capability, analytical approaches and the establishment of data bases have significantly improved the reliability of instrumentation and the possible accuracy of surface analysis. The significant contributions of Cedric Powell, Martin Seah along with those of many others provided the foundation for many of these advancements and served to establish many of the elements of surface analysis as it is currently practiced. From the prospective of the growth of the use of techniques such as XPS and based on the number of surface analysis systems available around the world, it is clear that use of the methods is increasing and many users are no longer experts. At the same time, many of the pioneering researchers who have made these advancements possible and who have the greatest knowledge about the techniques are at or nearing retirement age. Thus, we currently face two different but related challenges. First, we need to establish ways to efficiently transfer the important analytical knowledge to new and often less expert analysts. Second, new types of materials make additional demands on the analytical capabilities and it is important for a new generation of researchers to pick up the challenge. This talk will note some aspects of the progress and address the current challenges from the view of a nanotechnology project manager, the use of surface analysis in a DOE User facility (the Environmental Molecular Sciences Laboratory, EMSL), and from the view of a participant in two committees developing surface chemical analysis guides and standards. From the viewpoint of a project manager, it is useful to extract as much information as possible from the techniques being used. For some nanomaterials, this often requires application of multiple techniques, sophisticated analysis of some types of data and allowing the analysis of data from one method to inform the data collection and analysis of other types of data. In the EMSL we find that we are in a constant education mode teaching users about how to plan experiments, handle samples, collect and analyze data to obtain the desired information. The ASTM Committee E42 on surface analysis is currently working on a variety of consensus guides to enable new users to apply the experience of topical experts to analyze some type of samples and problems.

8:40am **AS-MoM3 Some Highlights and New Directions in  
Quantitative AES and XPS, C.J. Powell,** National Institute of Standards  
and Technology **INVITED**

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been productive tools for a large variety of scientific and technological purposes since commercial instruments became available almost 40 years ago. Elemental identification is relatively easy but quantitative measurements (e.g., identification of chemical state, determination of chemical composition, and measurement of film thicknesses) can be more difficult. I will give a brief overview of advances that have been made to calibrate instruments, assess surface sensitivity, and account for elastic scattering of the signal electrons. NIST databases are now available that provide XPS data, inelastic mean free paths, effective attenuation lengths (EALs), and elastic-scattering cross sections.<sup>1</sup> A new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) was recently released.<sup>1</sup> I will describe two applications of SESSA, one to assess the distinguishability of N composition profiles in SiON films on Si by angle-resolved XPS<sup>2</sup> and the other to determine EALs for photoelectrons in SiO<sub>2</sub>.<sup>3</sup> Small systematic differences between the SESSA results and experimental data give new insights into photoelectron excitation and transport. Finally, I will describe results from a VAMAS project to assess the magnitude of uncertainties in XPS peak intensities associated with different techniques and procedures for background subtraction.

<sup>1</sup> <http://www.nist.gov/srd/surface.htm>.

<sup>2</sup> C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 172101 (2006).

<sup>3</sup> C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 252116 (2006).

9:20am **AS-MoM5 The Bulk Ratio Method for Determining Surface  
Enhancement Using Auger Analysis, J.D. Geller,** Geller MicroAnalytical  
Laboratory, Inc.

Enhanced surface layers on stainless steel are engineered to provide improved corrosion resistance and reduced surface reactivity. Stainless steel can be electropolished and chemically treated in such a way that the surface finish is improved while enhancing the chromium levels near the surface. This modification is thought to increase corrosion protection and produce less gas stream particulates for semiconductor applications. The surface analysis techniques of x-ray photoelectron (XPS) and Auger electron spectroscopy (AES) have been used for decades to characterize the effects of these treatments by observing the near surface chemistry. International standards and practices (Sematech, ASTM F-1402-92 and SEMI 2335b), for AES and others for XPS, have been written to guide the analyst on how to calibrate their instruments, as well as collect and reduce the data. The test results most often examined are the oxide depth and maximum Cr to Fe ratio. Improved standard practices are necessary to reduce the variability that is seen between instruments and between laboratories for measuring the ratios. The variability likely stems from the use of sensitivity factors that are not representative of the host instrument and the improper selection of standards. The Bulk Ratio Method is a new approach which provides the same numerical value of chromium enhancement from data collected and reduced using either relative intensities or sensitivity factors. The Bulk Ratio can be easily calculated from historical data collected on different instruments and laboratories.

9:40am **AS-MoM6 Investigation of Average Matrix Relative  
Sensitivity Factors in Auger Electron Spectroscopy, M. Suzuki, K.  
Mamiya, N. Urushihara, N. Sanada,** ULVAC-PHI, Inc., Japan, **D.F. Paul,  
S. Bryan,** Physical Electronics

Auger electron spectroscopy (AES) is widely used for surface elemental analysis of the outer several nm of a material surface. Quantification is performed by converting signal intensities to elemental concentrations with relative sensitivity factors (RSFs). In practice, elemental RSF (ERSF) or atomic RSF (ARSF) tables are utilized in AES quantification. However, ISO18118:2004<sup>1</sup> recommends adopting an average matrix RSF (AMRSF), which includes corrections of matrix effects that are affected by elastic scattering, backscattering, inelastic mean free paths and atomic densities. In this study we calculate AMRSFs for the primary electron accelerating voltages of 3 kV, 5 kV, and 10 kV according to ISO18118 from experimentally obtained ERSFs. Comparing AMRSFs and ERSFs, there are greater differences for main group elements than for transition elements. For main group elements, AMRSF values are smaller than ERSFs for second row elements, while they inversely correlate for fifth and sixth row elements. So far, ERSFs for AES quantification have been provided as a database for primary electron energies less than 10 kV. Higher voltages, such as 20 kV or 30 kV, are in common use today in field emission AES instruments in order to achieve high spatial resolution. Thus RSFs for primary voltages higher than 10 kV are strongly desired for quantification of small areas. Therefore, we have extended AMRSFs for higher than 10 kV using Ichimura-Shimizu's backscattering factors<sup>2</sup> and Gryzinski's ionization cross-sections.<sup>3</sup> The former ones are assumed to be extrapolatable for higher than 10 kV.<sup>4</sup> In order to examine the validity of these calculations, experimentally obtained AMRSFs for 3 kV and 5 kV are compared with those calculated for 10 kV AMRSFs, showing good agreement. In the presentation, concentrations derived from AMRSFs will be compared with those from ERSFs for several kinds of compound materials.

<sup>1</sup> ISO 18118:2004, Surface chemical analysis - AES and XPS- Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials.

<sup>2</sup> S. Ichimura, R. Shimizu, and J. P. Langeron.

<sup>3</sup> M. Gryzinski, Phys. Rev. A336, 138 (1965).

<sup>4</sup> S. Tanuma, private communications. (to be submitted to J. Surf. Anal.).

10:20am **AS-MoM8 Quantitative Surface Chemical Microscopy, J.  
Walton,** The University of Manchester, UK **INVITED**

X-ray photoelectron spectroscopy is widely regarded as a mature technique, with a large instrument base, not restricted to specialist laboratories. One of the reasons for this is the apparent ease of quantification compared with other surface analytical techniques, and its ability to provide chemical state information. Yet comparison of quantified data between different instruments is still problematic. A procedure will be described for determining the instrument response function for selected modes of operation to allow quantification using theoretically determined sensitivity factors, enabling transfer of results between instruments. XPS is much less

frequently used in imaging mode, which was originally developed as a guide for small area analysis. However, the consequence of the acquisition of single energy images is that the aspects that make XPS spectroscopy appealing, i.e. ease of quantification and provision of chemical state information, are not available, since quantification requires peak area measurement after a suitable background subtraction and chemical state information is often dependent on resolution of overlapping photoelectron peaks. These limitations can be overcome by acquiring a spectrum at each pixel in an image, known as spectromicroscopy, so that the accepted processing procedures used in spectroscopy may be applied to the spectrum image data set. The acquisition of spectrum image data sets which may consist of 1000 images each containing 256 by 256 pixels presents further challenges for the analyst charged with the interpretation of thousands of spectra with low signal/noise. The use of multivariate statistical analysis to reduce the dimensionality of the data and to improve signal/noise will be demonstrated. Procedures will then be described to characterize the instrument performance in imaging mode, and to apply a modified quantification procedure to obtain atomic concentration images. Further, it will be shown that by maintaining the relationship between images and spectra so that pixels may be classified by chemistry, leads to improved curve fitting, and provides an alternative to multivariate curve resolution in visualizing physically meaningful spectra. Finally the ability to obtain spatially resolved nanostructural information will be discussed.

11:00am **AS-MoM10 Quantitative Characterization of Nb SRF Accelerator Cavity Surfaces Based on the Work of Seah and Powell, M.J. Kelley, H. Tian, College of William & Mary, C.E. Reece, Thomas Jefferson National Accelerator Facility**

In the very first figure in the first paper to appear in Surface and Interface Analysis, Seah and Dench displayed the kinetic energy dependence of the electron IMFP in solids. They and others, especially Cedric Powell, have pursued this issue relentlessly. Their work was seminal, pointing to the opportunity for non-destructive depth profiling by tracking emission from a particular element core level while varying photon energy. The opportunity was a motivation for construction of photoemission beamlines at synchrotron sources. We have used the soft x-ray undulator line (X1B) at National Synchrotron Light Source to study the near-surface structure of niobium. Niobium is the material of construction for superconducting radio-frequency (SRF) cavities at the heart of most new particle accelerators. The International Linear Collider is proposed to comprise some 16,000 Nb SRF cavities. The microwave rf penetrates only a few tens of nm into the Nb surface, lending great importance to optimizing it. Much is determined by the final post-fabrication steps, typically chemical etching or electropolishing followed by low temperature baking. While many characterization techniques can be applied, variable photon energy XPS has the added advantage that it does not alter the material examined. A specimen can therefore be examined at successive treatment stages, followed by SRF performance measurements.

11:20am **AS-MoM11 Formation of Ultra Thin Oxide Free Protective Coatings on Chromium and 316 L Stainless Steel from Etidronic Acid, S.L. Johnson, P.M.A. Sherwood, Oklahoma State University**

We have reported many examples of how thin (10nm or less) oxide free films can be formed on a number of metals. In this work we report how the use of etidronic acid (1-hydroxyethylidene-1,1-diphosphonic acid (hydroxyethyl diphosphonate or HEDP)) can form such films, providing an example of how an organophosphorus acid can form thin oxide free films in addition to the films previously reported for phosphorus acids. The films formed were produced on the surface of metallic chromium and on 316 L stainless steel by treatment by 3 molar etidronic acid using an anaerobic cell and a "bench" treatment. Core level and valence band X-ray photoelectron spectroscopy (XPS) were used to study the films formed. Compositional variations were interpreted through the use of band structure and X-alpha calculations. Valence band photoemission spectra interpreted in this manner were found to be effective in understanding subtle differences in the resulting surface chemistry as well as in identification of the various phosphates structures. The chromium foil experimental results indicate that the etidronate broke up and formed a phosphide on the surface. The anaerobic cell treatment of the chromium foil produced an extremely thin layer which consists of a phosphate which appears characteristic of chromium orthophosphate indicating that the etidronate molecule did not remain intact. Polished 316L stainless steel treated in 3 M etidronic acid formed a thin film when using the "bench" treatment, but a film characteristic of etidronate when the anaerobic cell was used. This thin etidronate film result shows that oxide-free etidronate films can be formed on stainless steel which may find application in implant fabrication.

11:40am **AS-MoM12 X-ray Photoemission Analysis of Chemically Treated CdZnTe Semiconductor Surfaces, A.J. Nelson, A.M. Conway, R.A. Bliss, C. Evans, J.L. Ferreira, R.J. Nikolic, S.A. Payne, Lawrence Livermore National Laboratory**

Device-grade  $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$  was subjected to various chemical treatments commonly used in device fabrication to determine the resulting microscopic surface composition/morphology and the effect on contact formation. Br:MeOH (2% Br),  $\text{N}_2\text{H}_4$ ,  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ , and  $(\text{NH}_4)_2\text{S}$  solutions were used to modify the surface chemistry of the  $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$  crystals. Scanning electron microscopy was used to evaluate the resultant surface morphology. Angle-resolved high-resolution photoemission measurements on the valence band electronic structure and Zn 2p, Cd 3d, Te 3d, O 1s core lines were used to evaluate the chemistry of the chemically treated surfaces. Metal overlayers were then deposited on these chemically treated surfaces and the I-V characteristics were measured. The measurements were correlated to understand the effect of interface chemistry on the electronic structure at these interfaces with the goal of optimizing the metal/ $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$  Schottky barrier for radiation detector devices.

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