Applied Surface Science
Room: 212D - Session AS-MoM

Quantitative Surface Analysis: Obtaining Quantitative Information in the Face of Material Complexity and Morphology Influences
Moderator: Christopher Szakal, National Institute of Standards and Technology (NIST), Alberto Herrera-Gomez, CINVESTAV-Queretaro, Mexico

8:20am AS-MoM1 Quantitative XPS of Core-Shell Nanoparticles, *Cedric Powell*, National Institute of Standards and Technology (NIST), *M. Chudzicki, W.S.M. Werner, W. Smekal*, Technical University of Vienna, Austria
We used the new version of the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1] to simulate XPS spectra of core-shell nanoparticles (NPs). Two series of simulations have been made. First, Cu 2p spectra were simulated using Al Kα x-rays for a monolayer of three types of Cu-Au NPs on an Si substrate: (a) an Au shell of variable thickness on a Cu core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm; (b) a Cu shell of variable thickness on an Au core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm; and (c) an Au shell of variable thickness on a 1 nm Cu shell on an Au core with diameters of 0.5 nm, 1.0 nm, 2.0 nm, 5.0 nm, and 10.0 nm. For these three morphologies, the outer-shell thickness was varied until the Cu $2p_{3/2}$ peak intensity was the same (within 2 %) as that found in our previous work with planar Cu/Au morphologies [2]. For each morphology, we performed simulations with elastic scattering switched on and off. We found that elastic-scattering effects were generally strong for the Cu-core/Au-shell and weak for the Au-core/Cu-shell NPs; intermediate elastic-scattering effects were found for the Au-core/Cu-shell/Au-shell NPs. The shell thicknesses required to give the selected Cu $2p_{3/2}$ peak intensity for the core-shell NPs were less than the corresponding film thicknesses of planar samples since Cu 2p photoelectrons can be detected from the sides and, for the smaller NPs, bottoms of the NPs.

Second, we determined effective attenuation lengths (EALs) for Cu $2p_{3/2}$ photoelectrons from NPs consisting of a Cu core of diameters 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm and a Cu shell with thicknesses between 0.25 nm and 3.75 nm. The EAL was determined from the Cu $2p_{3/2}$ intensity from the core with no shell and from the Cu $2p_{3/2}$ intensity from the core that was attenuated by a Cu shell of specified thickness. These EALs varied systematically with both Cu-core diameter and Cu-shell thickness. While the inelastic mean free path of Cu $2p_{3/2}$ photoelectrons (at 534 eV) in Cu is 1.12 nm, the EALs for a 10 nm Cu core varied from 0.53 nm to 0.65 nm as the Cu-shell thickness increased from 0.25 nm to 3.75 nm. In contrast, the EALs for a 0.5 nm Cu core increased from 0.78 nm at a shell thickness of 0.25 nm to a maximum value of 0.86 nm for a shell thickness of 0.75 nm and then decreased to 0.81 nm for a shell thickness of 3.75 nm. These changes show the important roles of NP morphology, NP dimensions, and elastic scattering in determining shell thicknesses by XPS.

[1] http://www.nist.gov/srd/nist100.cfm .

[2] C. J. Powell, S. Tougaard, W. S. M. Werner, and W. Smekal, J. Vac. Sci. Technol. A 31, 021402 (2013).

8:40am AS-MoM2 The Satellites of the 2*p* Core Level of Transition-Metals, *Alberto Herrera-Gomez*, CINVESTAV-Queretaro, Mexico
The shake-up satellites in XPS spectra are due to intrinsic energy losses as the photoelectron leaves the hosting atom. The first row transition metals, either in the metallic or in the oxide form (and sometimes in both), display clear shake-up features in the corresponding 2*p* core level. They are difficult to quantify because the shape of the main 2*p* peaks of these elements are highly asymmetric and the spectra contains a large background contribution. In fact, there is a frequent correlation between the presence of satellites and a large background intensity and, also, a large peak shape asymmetry. Through newly developed procedures it has been possible to properly fit all these core levels. In addition to those already described in the literature, the procedures allowed for pinpointing previously unreported shake-up satellites. A common feature of the satellites is that their spin-orbit splitting exhibits a remarkable difference with the associated to the main peak, suggesting angular-dependent correlation effects.

9:00am AS-MoM3 Quantitative Analysis of Advanced Commercial Glasses for Display Technologies, *Cody Cushman*, Brigham Young University, *N.J. Smith*, Corning, *T. Grehl, P. Bruener*, ION-TOF GmbH, Germany, *M.R. Linford*, Brigham Young University
A series of complex, multicomponent commercial glasses used in advanced display applications was exhaustively analyzed by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), low energy ion scattering (LEIS), Rutherford backscattering (RBS), atomic force microscopy (AFM), and spectroscopic ellipsometry, where the purpose of this study was to quantify the compositions and properties of these materials. XPS revealed the compositions of the upper ca. 10 nm of the glasses, which differed substantially from each other. Angle resolved XPS suggested some segregation of some elements to the surfaces. These results were confirmed by LEIS, which conclusively identified the elements at the true surfaces of the materials in a quantitative fashion. Like XPS, ToF-SIMS probed the near surface regions of the materials. However, it also identified elements that were beyond the detection limit of XPS. In addition, ToF-SIMS was used with XPS to quantitatively determine the concentration of –OH groups at the surfaces of the glasses via the $SiOH^+/Si^+$ ratio. Atomic force microscopy (AFM) showed that the materials were all extremely flat, with roughnesses on the order of 1 nm. Spectroscopic ellipsometry from 200 – 1700 nm was used to determine the optical properties (quantitative dispersion relationships) of the glasses. These techniques provided a comprehensive analysis of these glass samples. In addition, the glasses were subjected to various cleaning procedures (plasma, wet chemical cleans, etc.) and other surface treatments. The same suite of analytical techniques was then used to show conditions that led to changes or no changes in the compositions of the glasses, and these changes were quantified.

9:20am AS-MoM4 New Horizons in Practical Applications of Sputter Depth Profiling, *W.F. Stickle, C.N. Young, M.D. Johnson*, HP, *A.A. Ellsworth, Amy Walker*, University of Texas at Dallas
In the application of x-ray photoelectron spectroscopy the use of sputter depth profiling is one of the routinely used methods for analysis. Most industrial laboratories study a wide variety of material systems such as polymers or inorganic thin films and many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. Historically, mono atomic argon has been the ion source of choice in XPS, but even at low ion energies mono atomic argon will damage not only polymer systems converting them into amorphous carbon but also damage inorganic materials by creating, for example, intermediate oxides. In recent years other ion sources have become routinely available such as $C60^+$ and most recently, gas cluster ion sources. From a practical standpoint, i t is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a $C60^+$ ion gun for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include niobium oxides, titanium nitride and multilayer thin films.

9:40am AS-MoM5 ASSD 30th Anniversary Lecture: Sensitivity Factors in XPS: Where Do They Come From and How Accurate Are They?, *John Grant*, University of Dayton   **INVITED**
The most common method for quantitative analysis in X-ray Photoelectron Spectroscopy (XPS) incorporates relative sensitivity factors. In the 1970s and 1980s, several research groups studied the relative intensities of photoelectron lines and attempted to generate tables of relative sensitivity factors. Calculations were also made of ionization cross-sections using Mg and Al Kα x-rays, and experimental measurements were often compared to theory. The seminal measurements were made by Wagner and co-workers, who used two different types of electron energy analyzers from two different manufacturers and compared the results with theory and with other measurements. They found that the agreement in data from the two instruments on the same compounds was good, and they generated a table of empirically derived sensitivity factors. Today, many XPS analysts still use the relative sensitivity factors from Wagner's work, particularly if they use an instrument where the sensitivity factors were not provided. An early ASTM round-robin on XPS measurements on catalysts by 12 laboratories found a large spread in measured peak intensity ratios, even for instruments of the same manufacture, concluding that a calibration procedure for the intensity response of instruments was needed. A later ASTM round-robin

on pure Au and Cu concluded that the spread in intensity ratios was typically a factor of ten. Based on these results, Seah spearheaded studies on instrument transmission functions and developed a method so that the relative instrument response function between two different analyzers was better than 5%. In 1990, he published standard reference spectra for XPS and claimed all instruments may be calibrated absolutely to an accuracy of ± 2%. The National Physical Laboratory (NPL) developed and sold a procedure for generating an instrument transmission function, but it was not widely adopted. At least one manufacturer developed a model for measuring the transmission function in their instruments and measures it on each instrument before shipping it to the purchaser. A digital database of spectra was also developed at NPL, and could have provided a set of relative sensitivity factors for XPS, but it was never sold. It is important to know the origin of the sensitivity factors supplied by manufacturers and any limits placed on their applicability. By measuring spectra from a number of reference compounds one can quickly learn how reliable they are. For the most accurate measurements, one should measure relative sensitivity factors from standard compounds that match as closely as possible the compositions of unknowns.

10:40am   AS-MoM8   Ar⁺ and Cluster Ion Depth Profiling for Quantitative XPS Inorganic Thin Film Analysis, *Jennifer Mann, J.F. Moulder, S.R. Bryan, J.S. Hammond*, Physical Electronics
A successful XPS sputter depth profile should accurately identify layer thickness and composition of materials as a function of depth within film structures. In the case of inorganic thin films, monoatomic argon ion beam depth profiling continues to be the preferred choice despite issues with preferential sputtering, material migration, and chemical reduction that may occur during the sputter process to alter the apparent profile of the analyzed material [1-3].

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years provided the capability of successful depth profiling of polymer and organic materials as well as thin film structures while preserving the stoichiometry and chemical structures [4,5].

Currently, there is great interest in establishing the viability of these cluster ion sources as an alternative to Ar^+ ion beam sources for analyzing inorganic semiconductor and glass films, with particular interest in a possible improvement in the quantitative accuracy of the depth profile results compared to Ar^+ depth profiling [6,7].

The XPS depth profile of a thin film of the semiconductor material Indium Gallium Zinc Oxide (IGZO) was acquired with Ar^+, C_{60}^+ and GCIB ion guns. The film thickness and composition was characterized by RBS. Preferential sputtering of the In through the thin film depth profiles was observed with all three ion sources. The highest level of preferential sputtering of In was observed with the Ar^+ source while the C_{60}^+ source produced a relatively constant composition through the depth profiles and the most consistent with the expected elemental composition. The sputter volume per incident ion, the resulting interface width and the sputter crater roughness for the three different ion sources was also evaluated.

Similar evaluations for additional thin film oxide samples will also be presented. The results for these comparative studies suggest that depending on the composition of the inorganic oxide thin films, cluster ion sources may provide superior quantitative depth profiling for inorganic oxide thin film samples as well as organic thin film samples.

References

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[6] Y. Yamamoto, K. Yamamoto, *Mater. Sci. Eng.,* 2011, *18*, 022005.

[7] D. Kobayashi, Y. Yamamoto, T. Isemura, *Sur. and Inter. Anal.,* 2013, *45,* 113.

11:00am   AS-MoM9   Preservation of Chemical States in Mixed Material Surfaces when Profiling with Noble Gas Clusters, *Christopher Deeks, J.P.W. Treacy, P. Mack, T.S. Nunney*, Thermo Fisher Scientific, UK
The technique of X-ray Photoelectron Spectroscopy (XPS) is valued within the surface science community because it offers chemical quantification combined with surface specificity. The inherent surface sensitivity is due to the short mean free path of electrons (several nanometres) within solid media. Deducing the chemical composition of layers and interfaces at greater depths is achieved through milling the topmost layers by bombardment with argon ions. It has been well established, however, that milling with monatomic argon ions can cause sputter-induced damage at the surface, which in turn leads to a loss of chemical state information.

Surface etching with large clusters of argon enables the rapid collection of depth profiles from organic materials and removal of contamination from metal oxides while maintaining the chemical character of a material. Due to the relatively low energy per atom, however, the etch rates of most inorganic materials with these large clusters is not conducive to a high sample throughput. The implementation of smaller gas clusters allows higher energies per atom to be used, leading to increased rates of etching whilst preserving the chemical information that is lost when using monatomic argon.

Here we shall discuss how using a wider range of *ion energies per atom* enables more effective depth profiling of a wide variety of surface materials. We will present data from mixed inorganic and organic samples to show the benefits of these reduced cluster sizes.

11:20am   AS-MoM10   Photoemission from Complex Material Systems: Obtaining Quantitative Information, *Robert Opila, J. Church*, University of Delaware   **INVITED**
Photoemission is still a rapidly developing technique for surface analysis of complex systems using advancing physical and software technologies. In this talk we will consider two applications of electron spectroscopy taking advantage of hardware and software innovations.

Recently, the adaptation of XPS studies to synchrotron beamlines has produced a new technique – Variable Kinetic Energy XPS (VKE-XPS). VKE-XPS collects XPS data at multiple photon energies, and by doing so, also varies the likelihood of detection of electrons from buried layers. Compositional depth information can be extracted from VKE-XPS data sets by statistically sifting through the data using likelihood calculations assigned to each randomly generated depth profile. We have deployed a new algorithm, Bayes-Sim, which applies a Bayesian statistical approach to establish the framework for a belief system for each compositional simulation. Optimization of the search is carried out using a simulated annealing schedule, which assists in avoiding only locally optimized configurations. The Bayes-Sim algorithm has been encapsulated in a distributable, open-source graphical user interface J-FAB. These improvements were used to study high dielectric materials

Some of the most advanced chemical analytical techniques have been applied to study the degradation of paint pigments from artists in the post-impressionist era (late to early 20th century). The capability to investigate chemical speciation and elemental mapping in micro-samples is enabled only by the spatial resolution and high brilliance of synchrotron techniques like XANES and SR-FTIR. Fairly sophisticated data analyses for synchrotron beam lines have been encapsulated in easy to use software packages thereby complimenting the burgeoning field of art in science with the tools needed to tackle complex problems. In this work degradation of paintings by Munch and Matisse will be discussed.

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