Applied Surface Science Division
Room 204 - Session AS-MoM
Quantitative Surface Analysis

Moderators: Kateryna Artyushkova, University of New Mexico, Tim Nunney, Thermo Fisher Scientific, UK

8:20am **AS-MoM1 A Fistful of Data: The Good, the Bad and the Ugly of Quantitative Surface Analysis***, **Alexander Shard,*** National Physical Laboratory, UK **INVITED**

The properties of surfaces and interfaces govern the performance of most manufactured items, from advanced electronic devices, medical devices to packaging materials. The chemical analysis of such surfaces underpins the development of new products with better performance, ensures consistency in production and identifies the causes of failure. Commonly used methods, such as XPS and SIMS, can detect elements and chemical species, but also contain information on the amount of material and its distribution. This talk will describe the application of XPS and SIMS in the measurement of surface chemistry, highlighting the wealth of information available and the areas that need attention and development.

The measurement of coating thickness and the identification of defects is of major importance and will be a focus of attention. For thin (<10 nm) oxide films on silicon, XPS has been shown to be the most accurate method for such measurements and relies on a length scale that must be established by comparison with other methods. The applicability of XPS to other materials, non-planar samples and thicker films has improved in recent years and these developments will be described along with the potential use of both the inelastic background shape and HAXPES to extend the information depth, in some cases to more than 100 nm. The use of SIMS to measure surface composition is a particular priority, particularly in organic materials. Recent descriptions of matrix effects have highlighted the potential magnitude of this problem, but also point to methods to mitigate it. Although matrix effects are often taken into account when attempting to perform quantitative chemical analysis, their effects in SIMS images and depth profiles are often ignored but can be of overwhelming importance.

Recent international inter-laboratory studies have demonstrated that there can be significant disparity in the quantitative results reported by laboratories analysing the same materials using these techniques. The major causes of this variability will be discussed and shown to be predominantly due to the use, or misuse, of interpretational algorithms and reference data. The talk will highlight the role of ISO TC201 and VAMAS TWA2 in improving comparability and reproducibility in the results of these analytical methods.

9:00am **AS-MoM3 XPS and the Reproducibility Crisis***, **Donald Baer**, M.H. Engelhard,* Pacific Northwest National Laboratory

There is a growing awareness of reproducibility issues in many areas of science, including those associated with the AVS. In a 2016 survey of 1576 scientists reported in Nature (533 (2016) 452-454), 90% of those interviewed indicated that there was at least some level of reproducibility crisis in the scientific literature and more than half indicated that the crisis was significant. Data reproducibility and replication issues appear to be systemic and occur at multiple levels in the scientific process (in addition to fraud which is real but infrequent and not the focus here) including: i) within in a single study (Are results within one study appropriately reproducible, internally consistent, and adequately reported?), ii) within a laboratory (Have research groups established clear procedures and protocols to pass on to others the details needed for reproducing materials or other aspects of research?), iii) in reported results (Are measurement approaches and information in publications adequately detailed so that others could reproduce the work?). As the most commonly applied surface analysis method, use (or misuse) of XPS is a contributor to reproducibility issues but XPS is also an important tool that can be used to address some of the problems. Because of the high importance of the surface composition and chemistry on behaviors of materials as well as in biological and environmental systems, the use of XPS has been increasing for at least two decades. In the area of nanoparticles, lack of surface characterization is one source of material non-reproducibility. However, many researchers lack the experience or expertise needed to obtain the information sought from XPS measurements in useful and reproducible ways. Multiple types of problems appear and many of them can be observed in the literature including: analysis of samples at an inappropriate times or in non-optimal conditions; inappropriate handling and preparation of samples; damage to samples during analysis leading to faulty conclusions; incorrect or inconsistent quantification and/or spectral interpretation; lack of calibration and/or incorrect instrument set up; chemically meaningless fitting of data; inadequate reporting of methods, processes and results. This talk highlights examples of where XPS has been a tool for addressing reproducibility challenges, show a few examples of problem areas and summarize actions that the AVS is undertaking to help address reproducibility issues.

9:20am **AS-MoM4 Rapid Calculation Method of the Voigt Function for Use in the Analysis of Photoelectron Spectroscopic Data***, **Peter Sherwood**,* University of Washington

The basic shape of a photoelectron peak is Lorentzian, which is modified by instrumental and other factors, such as phonon broadening, to give a Gaussian contribution resulting in a peak shape that is a convolution of a Gaussian and a Lorentzian peak shape. The use of the correct peak shape is important in the analysis of photoelectron spectroscopic data. X-ray photoelectron spectra (XPS) from the core region often contain overlapping peaks which can be analyzed by fitting the experimental spectrum to a spectrum generated by the sum of a series of functions, each of which represent the individual peaks together with a background function.[1] XPS from the valence band region can be interpreted by calculating a spectrum from an appropriate model for the solid under study such as a band structure calculation, an approach which requires the inclusion of the photoelectron peak shape in order to correctly model the experimental spectrum.[2]

The Voigt function is a convolution of a Gaussian and Lorentzian and is the best representation for photoelectron peaks. Unfortunately the Voigt function cannot be represented directly as an analytical function and has to be evaluated numerically. Analytical functions were developed to approximate the Voigt function, and a number of so-called pseudo-Voigt functions have been developed. Analytical functions and their partial differentials can be calculated rapidly. One of the early pseudo-Voigt functions was a product function published by the author in 1979.[3]

The presentation will focus on how the true Voigt function can be rapidly calculated at speeds that are comparable to the calculation of pseudo-Voigt functions, with CPU times of a fraction of a second for complex curve fitting calculations on computers using Intel Core i7 processors.[4] The approach is based on the extensive work on the Voigt function by the atmospheric sciences community. Examples will be provided showing the application of the true Voigt function to the curve fitting of experimental core XPS data and the modelling of experimental valence band XPS data.

Reference

1.P.M.A. Sherwood, *J. Vacuum Sci. Technol.***1996**, *A14*, 1424.

2. P.M.A. Sherwood, *J. Vacuum Sci. Technol.***1997**, *A15*, 520.

3. R.O.Ansell,T.Dickinson,A.F.Povey,and P.M.A.Sherwood, *J. Electroanal. Chem.* **1979,** *98*, 79.

4. P.M.A. Sherwood, *submitted for publication.*

9:40am **AS-MoM5 Statistical Analysis and Peak Fitting of X-ray Photoelectron Spectroscopy Data. Good Practices and Procedures for Working up this Information.***, **Matthew Richard Linford**, V. Jain,* Brigham Young University

Determining appropriate methods of peak fitting X-ray photoelectron spectroscopy (XPS) data remains an active area of research. In this talk we discuss some of our recent efforts to better understand and interpret XPS narrow and survey scans. These include a description and comparison of the Gaussian-Lorentzian sum (GLS) and product (GLP) functions and their use in XPS peak fitting. This discussion will include a description of the shapes of the GLS and GLP as a function of the mixing parameter in their definitions and a comparison of these functions to the Voigt function. We will also discuss uniqueness plots as used to identify fit parameter correlation, width functions for identifying changes in peak envelopes, and principal components analysis, multivariate curve resolution, and pattern recognition entropy for studying and comparing series/groups of spectra. Finally, we also hope to briefly mention the importance of other statistical tools for better understanding XPS peak fitting. These include using chi squared to compare fits, showing the residuals to identify poor fits and/or questionable parts of fits, showing the sum of the fit components as a comparison to the original spectra, and employing the Abbe criterion for identifying correlated residuals.

10:00am **AS-MoM6 Modeling the Shirley Background***, **Alberto Herrera-Gomez**, D. Mulato-Gomez,* Cinvestav-Unidad Queretaro, Mexico*; A.D. Dutoi,* University of the Pacific

In quantitative chemical studies employing X-ray photoelectron spectroscopy, the total background signal can be well described as the sum of two terms, one originated from inelastic electron-energy losses and another that is expounded by the empirical Shirley method [1,2]. The inelastic part is very well quantified by the Tougaard theory proposed in 1982 [3]; the Shirley part, in the near-peak region, can be quantified by the method illustrated by Proctor and Sherwood [4]. Since the Tougaard background meets the experimental signal at binding energies ~ 50 or 100 eV above the peak, the Shirley contribution must banish at those energies. Therefore, the Shirley signal begins as a step-like function at the peak position to then vanish at higher binding energies (examples of the Shirley-signal in the entire range will be presented).

We showed that the Shirley part of the background is related to the capture of photons by deeper levels [5]. The physical process can be described as interchannel coupling [6] but adding a strong involvement of the valence band, i.e., a process resembling off-resonant participator photoemission with the generation of a shake-off type signal. Based on this model, we will present an approximate method to estimate the Shirley signal in the near-peak region.

[1] A. Herrera-Gomez, M. Bravo-Sanchez, F.-S. Aguirre-Tostado, M.-O. Vazquez-Lepe, The slope-background for the near-peak regimen of photoemission spectra, J. Electron Spectros. Relat. Phenomena. 189 (2013) 76–80. doi:10.1016/j.elspec.2013.07.006.

[2] A. Herrera-Gomez et al. Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. 46 (2014) 897–905. doi:10.1002/sia.5453.

[3] S. Tougaard, P. Sigmund, Influence of elastic and inelastic scattering on energy spectra of electrons emitted from solids, Phys. Rev. B. 25 (1982) 4452–4466. doi:10.1103/PhysRevB.25.4452.

[4] A. Proctor, P. Sherwood, Data analysis techniques in x-ray photoelectron spectroscopy, Anal. Chem. (1982) 13–19.

[5] A. Herrera-Gomez et al., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. doi:10.1002/sia.6364.

[6] E.W.B. Dias, H.S. Chakraborty, P.C. Deshmukh, S.T. Manson, Breakdown of the Independent Particle Approximation in High-Energy Photoionization, Phys. Rev. B. 78 (1997) 4553–4556.

10:40am **AS-MoM8 XPS Spectra and Bonding In Ionic Transition Metal Compounds***, **C. Richard Brundle**,* C. R. Brundle and Associates*; P.S. Bagus,* University of North Texas

In previous work, [1-3] it has been shown that the cation 2p XPS can reflect the extent of the covalent bonding between the metal cation and the ligands in formally fully ionic TM compounds (ie a nominal "oxidation state"). In the present work, the dependence of the 3p XPS on the covalent character and the charge state of the cation is compared to 2p for selected oxides and halides. The objective is to determine the extent to which the 3p XPS can be used to identify the open shell occupation of the cation; i.e., the nominal oxidation state. It is also of concern to show how the covalent character of the compound modifies the 3p XPS from that for an ideal, isolated, atomic cation. The systems that have been examined include Mn and Fe oxides and halides which are compared with experiment, with each other, and with the calculated XPS of isolated Mn and Fe cations. For the theoretical results, ab initio wavefunctions, WF, have been determined and have been used to obtain the energies and intensities of the cation 2p and 3p XPS. The compounds are modelled with embedded clusters [4] and the WFs are solutions of the Dirac-Coulomb Hamiltonian. Implications for the limitations of quantitation, both elemental and chemical compound, using XPS peak intensities together with standards or theoretical cross-sections, are also discussed

1. C. J. Nelin, P. S. Bagus, C. R. Brundle, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. (to be submitted).

2. P. Bagus, C. R. Brundle, and C. J. Nelin, J. Chem. Phys. (to be submitted).

3. P.Bagus, C. R. Brundle, and C. J. Nelin, presented at the AVS International Symposium, 2017

4. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. , 273 (2013).

11:00am **AS-MoM9 Combinatorial Group XPS Analysis of Novel Material Systems***, **Sarah Coultas**,* Kratos Analytical Ltd, UK*; J.D.P. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Limited, UK

The combinatorial approach has been used widely to discover new material phases for many years now, allowing rapid exploration of composition–structure properties in complex material systems[1]. Compositional mapping is central to obtaining comprehensive pictures of material systems and mapping active chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical mechanism of the properties. Here we will apply the traditional approach of combinatorial techniques to explore several model systems using X-ray photoelectron spectroscopy XPS demonstrating the use of group analysis for two different application - ternary alloy formation post thin-film deposition and polymer microarray biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading onto more detailed bulk/surface comparison studies using depth profiling techniques. Combinatorial methods will also be exploited for screening of functional biomaterials. The surface composition of a series of polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the different systems as will illustrations and set analyses.

C. J. Long, J. Hattrick-Simpers, M. Murakima, R. C. Srivastava, I. Takeuchi, V.L. Karen and X. Li, *Rev. Sci. Inst.,* 78, 072217, 2007.

11:20am **AS-MoM10 Towards Spatially Resolved Quantification of Gold Nanoparticles Embedded in an Organic Matrix using Secondary Ion Mass Spectrometry***, **Shin Muramoto**, J. Bennett,* National Institute of Standards and Technology (NIST)

Secondary ion mass spectrometry (SIMS) has been successfully used to detect metal nanoparticles in a wide array of organic matrices such as in biological cells, tissue, and within polymer films. However, there are also instances when the nanoparticles cannot be detected at all, presumably due to a combination of charge competition with salts, sample charging, type of primary ion source, and ion dose density. For example, 150 nm Au nanoparticles (AuNPs) embedded in soil nematodes could easily be detected and resolved in a dynamic SIMS instrument using a Cs^+ ion source with a secondary ion yield of 10^{-12}, but no signal could be generated when a ToF-SIMS instrument equipped with a Bi_3^+ ion source was used, even when the sample was covered with a layer of Cs to enhance signal. To test what factors influence the ionization of AuNPs and to identify the ion dose density threshold for detection, a test sample was prepared through inkjet-printing of precisely measured amount of AuNPs onto porcine skin gelatin, a surrogate for biological tissue. By systematically changing the chemistry of the AuNP solution with solutes such as salts, it is possible to see their effect on nanoparticle ionization. The test sample can also be used for the quantification of nanoparticles by changing their concentrations, and see the effects of depth profiling in quantification by changing the distribution of nanoparticles in 3-dimensional space or position inside the film. The ultimate objective of this study is to create a test sample for the spatially resolved quantification of nanoparticles in a biologically relevant environment, to be able to quantify the number of particles in a given area without resorting to high lateral resolution instruments. The effort will also develop SIMS instrumentation into a tool that can be used for determining the pharmacokinetics and biodistribution of nanoparticles in tissue. Preliminary analysis using a ToF-SIMS instrument with a Bi_3^+ ion source showed that the mere presence of gelatin reduced the secondary ion yield of AuNPs by an order of magnitude. In addition, increasing the concentration of Na^+ from 10^{-6} M to 10^{-3} M led to a rather linear decrease in the secondary ion yield from 10^{-13} to 10^{-15}, consistent with the effect of salts on analyte response in an electrospray ionization system. [1] For the

dynamic SIMS, the presence of gelatin had no noticeable effect on secondary ion yield of the nanoparticles.

[1] Constantopoulos, T. L.; Jackson, G. S.; Enke, C. G. Effects of Salt Concentration on Analyte Response using Electrospray Ionization Mass Spectrometry. 1999, , 625-634.

11:40am **AS-MoM11 Correction-Free Analysis of SIMS Data at High Mass Resolution in the Presence of Detector Saturation***, **Lev Gelb**, A.V. Walker,*
University of Texas at Dallas

We present a strategy for analyzing TOF SIMS data sets affected by detector saturation at high mass resolution. The detectors used in many instruments undercount ions due to saturation effects; if two or more ions arrive within a very short interval (the “dead time”) only the first to arrive is recorded. This changes both the total number of ions collected and their statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed; at low masses the great majority of ions often go undetected. Methods are available for “correcting” the collected spectra at both unit-mass and high-mass resolutions based on an assumed model for the behavior of the detector, but these are problematic when the number of scans taken is small and/or the saturation is sufficiently high. Calculation of the variance of the corrected data as required in many multivariate analysis techniques is also complex. As a result, performing quantitative analysis of TOF SIMS data while preserving high mass resolution remains problematic.

Rather than attempt to correct the measured data to remove saturation, we incorporate the detector behavior into the statistical distribution used in maximum *a posteriori* reconstruction, justified on Bayesian grounds. Essentially, this method finds the *most probably correct* spectra, given the observed data and available prior information. This approach has several advantages over previous techniques: no approximations are involved other than the assumed model of the detector, the method performs well even when applied to highly saturated and/or single-scan data sets, and it is possible to calculate uncertainty estimates for the extracted quantities. Our method is first demonstrated by application to individual spectra. The correctness of the approach and its efficacy are demonstrated on synthetic data sets, and then applied to selected experimental results. Performance on data of different degrees of saturation and/or total number of counts is determined and compared with existing correction-based approaches; the effects of dead-time duration on lineshape and FWHM are also explored. We then demonstrate extension of this approach to imaging data and compare and contrast the results obtained with analyses performed at unit-mass resolution.

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