

# Monday Afternoon, October 19, 2015

## Applied Surface Science

Room: 212D - Session AS-MoA

### Practical Surface Analysis I: Interpretation Challenges

**Moderator:** Karen Gaskell, University of Maryland, College Park, Alan Spool, HGST, a Western Digital Company

2:20pm **AS-MoA1 ASSD 30th Anniversary Lecture: XPS: Three Challenges and an Opportunity, James Castle**, University of Surrey, UK  
**INVITED**

The 3 challenges refer to ambitions that have been on the books for many years.:

**1**, to obtain XPS data from individual sub-micro particles using a laboratory instrument. Cazaux (1975) scanned an electron beam across the reverse of an Al foil holding the particles. A similar arrangement was adopted by Jenkins and Castle (1994). Their object was to examine the interface region of microtomed thin sections of adhesive joints. Useful parameters were determined but this, reverse-side excitation of x-rays is not easily adapted for use in a laboratory instrument. Recently Castle et al(2013) have returned to the subject using an Auger spectrometer. The particles are scattered on Al or Mg foil from which X-rays are produced by the impact of an electron beam close to the particle. Examples will be given

**2**, the need to make the Auger Parameter (AP) more intuitive. The AP, Wagner (1974), depends on the relaxation energy of the chemical structure. It is so easily determined but yields a number that is so readily forgettable! Mg has a value of 2488eV whilst Ca is 644eV. West and Castle(1982) showed how a universal scale for the AP might be produced. The zero point is that for a non-polarisable lattice. Since the refractive index (RI) also depends on lattice polarizability the zero-point can be found using the value of  $RI = 1$  on a suitable plot and thus elements placed on a common scale. More recently (2002), Castle et al used the method to compare AP'S for V and O for a series of compounds It is concluded that a universal scale would greatly benefit those in applied surface chemical analysis .

**3**, is codifying the procedures that would enable manufacturers to give a first estimate of near-surface structure from the survey scan: helping to plan the detail scans which follow the survey. Castle and Baker (1999) gave an indication of how this might be approached and a very detailed set of rules was published by Castle (2007) An ISO standard for recognition of a C1s peak as contamination is being developed by ISO TC201. With this, manufacturers should have the confidence that any automated data processing will have the backing of users.

The **opportunity** would bring to fruition the vision of those members of ASSD when they launched Surface Science Spectra as a Journal and a database in 1993. As a Journal it is still unique in our field and is much valued for its provision of reference spectra for materials of current interest. The opportunity is to provide a searchable data base of peak energies for all elements in the diverse set of 1000 materials included in the 22 volumes now available.

3:00pm **AS-MoA3 Results from a VAMAS Inter-Laboratory Comparison on the Measurement of Composition of Organic Mixtures in Depth Profiling, Alexander Shard**, National Physical Laboratory, UK

Argon cluster sources for 3D analysis of organic materials are starting to become routinely used in material analysis. Most new XPS and SIMS instruments are now equipped with such sources and are finding widespread use in both academia and industry. The purpose of a depth profile is to measure the distribution of chemical species and therefore it is important to assess the ability of various techniques and approaches to provide this information. One of the most popular analytical methods to combine with cluster beam sputtering is SIMS. This method provides excellent specificity, high sensitivity in most cases and enables discrimination of compounds that cannot be matched by other methods such as XPS. However, there are a number of factors that prevent organic SIMS from being quantitative. For XPS there is a well-established route to obtain chemical compositions, which is its primary advantage in organic depth profiling.

Until recently, organic SIMS data could be used to identify compounds, and could only measure concentrations in special cases. The major limiting factor in SIMS is the 'matrix effect' which has not been the subject of any substantive or coordinated investigation since the genesis of organic SIMS analysis in the 1980s. Fortunately, the ability provided by argon cluster sources to perform nearly damage-free profiles of organic materials allows us to begin to address this effect.

Mixed molecular materials of known composition have been made with sufficient precision and stability for a reliable analysis to be performed. The materials demonstrate, unambiguously, that matrix effects are significant in molecular SIMS experiments, but also that these effects can be measured and described. It is found that the matrix effects are remarkably consistent between laboratories and appear to depend upon two main factors: the identity of the secondary ion and; the analytical source used. Furthermore, it is possible to establish normalization schemes that compensate for the matrix effect whilst also eliminating the other major source of error in quantitative SIMS: instability and drift in the primary beam current.

This talk will describe VAMAS project A3(g), the SIMS matrix effect and implications in the quantitative analysis of SIMS depth profiles. These effects are not restricted to compositional analysis but also have a profound influence on the apparent position of interfaces, often contributing the major source of uncertainty to the measurement of the thickness of an organic layer.

3:20pm **AS-MoA4 In Operando Studies of High Temperature, Heterogeneous Electrocatalysis on a Lanthanum Strontium Manganite-based Solid Oxide Electrochemical Cell, Aaron Geller, B. Eichhorn**, University of Maryland, College Park

Near ambient X-ray photoelectron spectroscopy (APXPS) was used for *In Operando* studies on lanthanum strontium manganite (LSM,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3\pm z}$ ) electrodes, one of the most popular materials currently in use on solid oxide electrochemical cells (SOCs). SOCs consisting of two LSM electrodes on a yttria-stabilized zirconia (YSZ) electrolyte were probed in an oxygen atmosphere (0.5 Torr) at  $\sim 600^\circ\text{C}$  under open circuit voltage (OCV) and polarized conditions. Polarization promotes the oxygen reduction reaction (ORR, cathodic reaction) on one LSM electrode and oxygen evolution reaction (OER, anodic reaction) on the other. Through use of an area detector, electrochemically-induced phenomena on the surface of the cell such as surface potential mapping, Sr segregation, and changes in the Mn oxidation state were observed and spatially resolved to within 20 microns.

By tracking shifts in the La 4d and Sr 3d peaks under polarization relative to OCV, local surface potentials of each LSM electrode were determined and it was observed that the majority of electrochemical activity, signified by a sharp potential drop, was located at the LSM/YSZ interface (shifts in the Zr 3d peaks were used to determine the local potential of YSZ). Several challenges in interpretation were found, the most surprising of which was a potential separation between the lanthanum and strontium components of the LSM lattice which were expected to exhibit the same potential under bias. Instead, the lattice La was driven to a higher potential than the lattice Sr on both electrodes. Furthermore, it was found that lattice Sr was relatively depleted under bias on each electrode, though the effect was more pronounced on the OER side. Sr 3d spectra also showed two different species under bias, lattice Sr and surface-segregated SrO, with the surface species shifted to a higher potential than the lattice Sr species. The data analysis process of these complex systems presented several challenges as well, which will be discussed.

3:40pm **AS-MoA5 Building the Link Between XPS Data and Functional Properties of Materials, Kateryna Artyushkova, I. Matanovic, S. Kabir**, University of New Mexico, B. Kieffer, New Mexico State University, A. Serov, P. Atanassov, University of New Mexico **INVITED**

Building structure-to-property relationships is one of the most often attempted research tasks in today's chemistry of materials. Often relationships are directly dependent and easy to identify. In complex, nano-structured functional materials, those correlations are intertwined and multi-directional. Predicting macroscopic property of interest, such as activity, wettability, stability, etc., based on correlation with materials surface chemistry is challenging but yet accomplishable.

The relationship between functional property and the chemical structure of materials is typically established through correlations between performance metrics parameters and various spectroscopic techniques, including XPS, XANES, XPES, TOF-SIMS, and Mössbauer spectroscopy. The primary advantage of XPS in the characterization of heterogeneous multicomponent nanostructures is the ability to discriminate between different surface oxidation states and chemical environments. However, the assignment of XPS peaks in highly heterogeneous materials is not straightforward. A significant improvement in the assignment of peaks at various binding energies could be achieved using reference materials, yet, many relevant reference materials do not exist. State-of-the-art computations allow the determination of BE shifts for specific defect chemistries and geometries, providing valuable information for processing and interpretation of spectra data.

In this talk, I will discuss approaches towards structure-to-property relationships derived for energy-related materials, such as electrocatalysts for fuel cell and biocatalysts for microbial fuel cells. I will discuss multivariate approaches towards correlating XPS data with performance characteristics and binding energy shift calculations using DFT for interpreting XPS spectra. Application of XPS instrumentation with in-situ capabilities to study materials under conditions relevant to their application will be also discussed.

**4:20pm AS-MoA7 Multitechnique Characterization of Protein G B1 Orientation on Surfaces, Elisa Harrison, G. Interlandi, D.G. Castner, University of Washington**

The orientation of adsorbed proteins on surfaces has been shown to influence biological responses, so research and development of biotechnological applications (e.g., sandwich ELISAs) have focused on controlling the orientation of each protein layer. However, characterizing protein orientation has been a challenge. The goal of this research is to address these challenges by developing methodology to study multilayer protein systems. Specifically, we aim to determine the orientation of protein G B1, an IgG antibody-binding domain of protein G, on various surfaces and the effect of its orientation on antibody binding using a variety of surface-sensitive tools and simulations. We propose that binding selectivity will increase for well-ordered protein films due to high availability of binding domains. To achieve control over surface properties, we have utilized four types of self-assembled monolayers (SAMs) to control protein orientation: N-Hydroxysuccinimide-terminated SAMs and dodecanethiol SAMs to immobilize protein G B1 in a random orientation and maleimide-terminated SAMs and bare gold to immobilize cysteine mutants of protein G B1 in a well-ordered orientation. Developing methods using surface-sensitive, label-free tools, such as XPS, ToF-SIMS, and quartz crystal microbalance with dissipation monitoring, provide detailed information of the adsorbed proteins, such as composition, coverage, and orientation. Additionally, computational methods to predict the orientation of proteins on surfaces can help to interpret and complement experimental techniques. In this work, we describe the development of a simulator to determine protein orientation on a surface using Monte Carlo (MC) simulations. We chose two proteins to test the MC simulator: LK $\alpha$ 14 peptide and protein G B1. We chose LK $\alpha$ 14, a 14-mer consisting of only leucine and lysine amino acid residues, as a benchmark because of its predictable structure and orientation on hydrophobic surfaces. To test the MC simulator on a more complex system, we used protein G B1. Preliminary MC simulations show that protein G B1 is likely to interact with a graphene surface through residues Met1, Val21, Ala48, and the hydrophobic part of Lys10 on terminal ends of the protein. We will extend the MC algorithm to predict the orientation of additional protein/surface combinations and validate using experimental results. While the systems explored thus far are model systems that are far less complex compared to biological systems of the real world, we aim to develop methodology using state-of-the-art tools that can be continuously improved to help expand our knowledge of, and possibly control, biomolecules on surfaces.

**4:40pm AS-MoA8 Investigation of Composition and Structure of Functionalized Carbon Materials, Svitlana Pylpenko, K.N. Wood, Colorado School of Mines, A.A. Dameron, National Renewable Energy Laboratory, R. O'Hayre, Colorado School of Mines**

While significant efforts have been placed on understanding the role of nitrogen in real, application based environments utilizing high surface area carbon supports, a lack of knowledge exists in understanding the specific functionalities and their role in improving performance. In this work we expand the understanding of nitrogen functionalized high surface area carbon supports by focusing on the careful analysis of the distribution of nitrogen functionalities through XPS and other complementary techniques, such as Raman and NEXAF spectroscopies. Functionalization of several high-surface carbons was performed using nitrogen ion implantation using a variety of ion implantation parameters. The results contained herein show that increasing implantation time only marginally elevates nitrogen concentration, forming mostly single defect structures. Increasing the beam current results in formation of more complex defect structures containing clustered multi-nitrogen defects, similar to those observed in carbon nitride materials. We also show that higher nitrogen dosage levels create a more homogeneous distribution of nitrogen functionalities, regardless of initial carbon material or the resulting nitrogen concentration.

**5:00pm AS-MoA9 How to Make Amorphous Carbon Stable: An In Situ XPS and NEXAFS Investigation of Thermally-Induced Structural Evolution of Amorphous Carbon Surfaces, Filippo Mangolini, Ecole Centrale de Lyon - LTDS, France, J. Hilbert, J.B. McClimon, J.R. Lukes, R.W. Carpick, University of Pennsylvania**

Silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) coatings are fully amorphous thin-film materials consisting of two interpenetrating

networks, one being a hydrogenated amorphous carbon (a-C:H) network and the other a silica glass network. At temperatures above 150°C, pure a-C:H films undergo a rapid degradation that starts with the evolution of hydrogen and is followed by the conversion of sp<sup>3</sup> bonds to sp<sup>2</sup> [1]. However, a-C:H:Si:O exhibits much lower susceptibility to oxidative degradation, and higher thermal stability compared to a-C:H. This makes a-C:H:Si:O attractive for many applications, including next generation hard disk drives, which require overcoat materials that are thermally stable up to temperatures above 500°C. Although it is well-established that a-C:H:Si:O possesses superior thermal stability and oxidation resistance relative to a-C:H, the scientific basis for this behavior is not understood. To investigate this, a combined *in situ* X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy study was performed. Changes in the surface chemistry and bonding configuration of a-C:H:Si:O (e.g., silicon oxidation state, carbon hybridization state) were accessed *in situ* at temperatures up to 450°C. A novel methodology for processing NEXAFS spectra, which makes it possible to account for the presence of a carbonaceous contamination layer on an air-exposed material, was developed [2]. This allowed quantitative evaluation of the carbon hybridization state in the film as a function of the annealing temperature. Upon high vacuum annealing, two thermally-activated processes could be determined to take place in a-C:H:Si:O by assuming a Gaussian distribution of activation energies with mean value  $E$  and standard deviation  $\sigma$ : a) ordering and clustering of sp<sup>2</sup> carbon ( $E \pm \sigma = 0.22 \pm 0.08$  eV); and b) conversion of sp<sup>3</sup>- to sp<sup>2</sup>-bonded carbon ( $E \pm \sigma = 2.7 \pm 1.0$  eV). The experimental results are in qualitative agreement with the outcomes of molecular dynamics simulations performed using the ReaxFF potential. To determine the environmental dependence of the surface structural evolution of a-C:H:Si:O, the results of the *in situ* XPS/NEXAFS investigation were compared to those for a-C:H:Si:O samples heated in air, showing a strong effect of atmospheric oxygen. These results provide guidance for designing modified materials able to meet ever-increasing performance requirements of coatings for demanding applications.

1. F. Mangolini, F. Rose, J. Hilbert, R.W. Carpick, Applied Physics Letters, 103, 161605, 2013

2. F. Mangolini, J.B. McClimon, F. Rose, R.W. Carpick, Analytical Chemistry, 86, 12258, 2014

**5:20pm AS-MoA10 A Comparative Study of the Native Oxide on 316L Stainless Steel by XPS and ToF-SIMS, Sabrina Tardio, M.-L. Abel, University of Surrey, UK, R.H. Carr, Huntsman PU, J.E. Castle, J.F. Watts, University of Surrey, UK**

AISI 316L is an austenitic stainless steel which is widely used in applications that require a degree of resistance to crevice and/or pitting corrosion. The L identifier of 316L indicates lower carbon content than the standard 316 grade, a characteristic which reduces the susceptibility to sensitization (grain boundary carbide precipitation) and for this reason it is widely used in heavy gauge welded components. The corrosion resistance of stainless steel is a result of the presence of a thin oxide layer on its surface. The passivation of stainless steel takes place in atmospheric conditions which yields a film that is self-healing on localised damage. The oxide, naturally formed in the atmosphere, is generally referred to as the native oxide and it is affected by environmental factors and, for that reason, different methods are often employed to modify the oxide layer to make it suitable for particular applications. This steel is also widely used as a substrate for adhesion; it is one of the "technological surfaces" on which organic coatings are applied. In this context, differences in the chemistry of the surface, as a consequence of different treatments, will influence the degree and modality of interaction of the adhesives with this metal. Many works have studied stainless steel with the aim of understanding more about the modification of this oxide layer, but few have addressed the composition of the passive film in its air-formed or water exposed state. In this work, attention is focused on the composition of the native oxide and changes in its chemistry brought about by water exposure. The native oxide film on stainless steel is very thin, of the order of 2 nm, and known to be readily modified by immersion in aqueous media. In this paper, XPS and ToF-SIMS are employed to investigate the nature of the film in the air-formed and water emmersed states. The film is described in terms of oxide, hydroxide and water content. The preferential dissolution of iron is shown to occur on immersion. It is shown that a water absorbed layer and a hydroxide layer are present above the oxide-like passive film. The concentrations of water and hydroxide appear to be higher in the case of exposure to water. A secure method for the peak fitting of Fe2p and Cr2p XPS spectra of such films on their metallic substrates is described. The importance of XPS survey spectra is underlined and the feasibility of C<sub>60</sub><sup>+</sup> SIMS depth profiling of a thin oxide layer is shown.

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