

Monday Morning, November 10, 2014

Applied Surface Science

Room: 316 - Session AS+MC-MoM

Quantitative Surface Analysis

Moderator: James A. (Tony) Ohlhausen, Sandia National Laboratories, William Stickle, Hewlett Packard

8:20am **AS+MC-MoM1 Automating Multi-Technique Surface Analyses for Materials Characterisation**, *Andrew Wright, P. Mack, T.S. Nunney, A. Bushell, A. Yeadon*, Thermo Fisher Scientific, UK

X-ray photoelectron spectroscopy (XPS) is a well-established technique that has become a cornerstone of surface analysis due to the wealth of chemical bonding information that it provides. Many other surface sensitive techniques exist, of course, and often can be found on the same instrumentation. Ultraviolet photoelectron spectroscopy (UPS) provides detailed valence electronic structure information. Reflection electron energy loss spectroscopy (REELS) can yield hydrogen quantification, shake-up transition and band gap information. Ion scattering spectroscopy (ISS) offers the most surface-sensitive probe of composition. Auger electron spectroscopy (AES) offers chemical information with high spatial resolution. In addition, monatomic and cluster ion beams can be used in concert with these methods for cleaning or depth profiling.

The various techniques can each provide important information in isolation, but the real power of surface analysis comes from combining these analyses of a sample and correlating the information to provide a more thorough characterisation of the material. Traditionally, however, switching between techniques has been difficult or laborious, and this has tended to deter analysts from performing multitechnique studies. Improvements to automation and usability are vital for bringing the less-used methods into common practice.

This paper presents several multitechnique surface analyses of samples in a single instrument (the Thermo Scientific Escalab250Xi), showing how automated, sequential applications of these complementary chemical, electronic and structural characterisation methods can be applied to polymeric, catalyst, photovoltaic and semiconductor materials, yielding valuable results with minimal effort.

8:40am **AS+MC-MoM2 The S' component in the Si 2p X-ray Photoemission Spectrum of Si [001]**, *Alberto Herrera-Gomez*, CINVESTAV-Queretaro, Mexico, *M.O. Vazquez-Lepe*, Universidad de Guadalajara, Mexico, *P.G. Mani-Gonzalez*, Universidad Autónoma de Ciudad Juárez, Mexico, *O. Ceballos-Sanchez*, CINVESTAV-Queretaro, Mexico

Because of the technological relevance of the Si [001] surface, the Si 2p is one of the most studied core levels with laboratory X-Ray Photoelectron Spectroscopy (XPS). An important application is the quantification of the thickness of oxide layer, which is done by comparing the intensity of the substrate and Si⁴⁺ components. Peak-fitting is usually done by employing one doublet for the substrate and another for the Si⁴⁺ shifted around 3.5 or 4 eV to higher binding energy (from the substrate). In detailed studies, the quantification of the suboxides is usually done employing components, originally proposed by Himpfel et al.,¹ with the following shifts: 2.5 eV for Si³⁺, 1.75 eV for Si²⁺, and 0.95 eV for Si¹⁺. A proper fit, besides those five components, actually requires a six component shifted by approximately 0.3 eV. This peak has been clearly identified in various synchrotron studies such as that by Landemark et al.,² where it is referred as S'. In that study, and in others, it is assigned to one monolayer (the second) of the substrate. Although clearly present in Si 2p spectra obtained with laboratory XPS equipped with monochromatized Al K α radiation, this component is largely unspoken in the literature. In one of the few studies that mention its existence it is assigned to an asymmetry of the bulk peak.³ In this presentation it is going to be shown that this interpretation is inconsistent with the angular dependence observed by S'. The physical origin of S', which is going to be discussed in detail, goes in a direction compatible with that proposed by Landemark et al.: although it represents one monolayer for the clean Si [001] surface, for oxide-covered surfaces it corresponds to a few monolayers of the substrate.

[1] F. J. Himpfel, F. R. McFeely, A. Taleb-Ibrahimi, and J. A. Yarmoff, *Phys. Rev. B* 38, 6084 (1998).

[2] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, *Phys. Rev. Lett.* 60, 1588 (1992).

[3] D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi and I. V. Mitchell. *Surf. Inter. Anal.* 21. 44-50 (1994).

9:00am **AS+MC-MoM3 Quantitative Analysis of Nanostructured Surfaces by means of X-ray Photoelectron Spectroscopy: Theory and Applications**, *Wolfgang Werner*, Vienna University of Technology, Austria **INVITED**

The theory of signal emission in electron spectroscopy is discussed on the basis of the so-called Landau-Goudsmit-Saunderson (LGS) loss function, which leads in a natural way to rigorous spectrum analysis techniques, the so-called partial intensity analysis (PIA). Examples of applications include theoretical calculation of model spectra as well as analysis of experimental spectra using of X-ray Photoelectron Spectroscopy (XPS) and Reflection Electron Energy Loss Spectroscopy on nanostructured surfaces [1], the contribution of in-vacuo electron scattering to electron spectra [2] and secondary electron-electron energy loss coincidence spectroscopy (SE2ELCS) [3]. In the latter technique correlated electron pairs are analysed and detected, thereby giving unique insight into the dielectric properties of a solid.

A layered electron gas system will be considered as an important case study for quantitative surface analysis: it is shown how single layer graphene data can be extracted from measurements on macroscopic three dimensional highly oriented pyrolytic graphite (HOPG) samples. After appropriate analysis, a feature in the spectrum can be identified which quantitatively correlates with the sp²-content in arbitrary carbon samples, as follows from comparison with Raman measurements.

[1] W S M Werner, *Surf. Interf. Anal.* 31(2001)141

[2] Werner, Wolfgang S. M., Novak, Mihaly, Salvat-Pujol, Francesc, Jiricek, Petr, Zemek, Josef, *PRL* 110(2013)086110

[3] W. S. M. Werner, F. Salvat-Pujol, A. Bellissimo, R. Khalid, W. Smekal, M. Novak A. Ruocco and G. Stefani, *Phys. Rev. B* 88(2013)201407

9:40am **AS+MC-MoM5 Effective Attenuation Lengths for Hard X-ray Photoelectron Spectroscopy (HAXPES)**, *A. Jablonski*, Polish Academy of Sciences, Poland, *Cedric Powell*, National Institute of Standards and Technology (NIST), *S. Tanuma*, National Institute for Materials Science (NIMS), Japan

HAXPES is now being used to characterize thicker overlayer films than is possible with conventional XPS using Al and Mg K α x-ray sources. As a result, there is a need for effective attenuation lengths (EALs) to determine film thicknesses at electron energies larger than about 1.5 keV. Jablonski and Powell [1] published a simple practical EAL expression from fits to EALs calculated from solution of the kinetic Boltzmann equation within the transport approximation for electron energies between 61 eV and 2 keV and photoelectron emission angles between 0° and 50°. This approach has now been extended to electron energies up to 5 keV with account also taken of non-dipole terms in the photoionization cross section. EALs have been calculated for Si 1s, Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} photoelectrons excited by Mg K α , Al K α , Zr L α , and Ti K α x rays using the inelastic mean free paths of Tanuma *et al.* [2] for each solid. EALs from the non-dipole approximation were up to about 2% larger than those from the dipole approximation. Good agreement has been found between the new EALs and EALs determined from Monte Carlo simulations and from the NIST SESSA database [3]; with the latter database, simulations can be made for photoelectron energies up to 20 keV. We found that the new EALs were also consistent with the previous expression [1]. Finally, the new EALs are reasonably consistent with the EALs measured by Sacchi *et al.* [4] for Co, Cu, and Ge but there was poorer agreement with the EALs measured by Rubio-Zuazo and Castro [5] for Au. Disagreements between the calculated and measured EALs for Au at energies less than 5 keV were attributed to non-ideal morphologies of the thinner Au films.

[1] A. Jablonski and C. J. Powell, *J. Vac. Sci. Technol. A* 27, 253 (2009).

[2] S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* 43, 689 (2011).

[3] <http://www.nist.gov/srd/nist100.cfm>.

[4] M. Sacchi *et al.*, *Phys. Rev. B* 71, 155117 (2005).

[5] J. Rubio-Zuazo and G. R. Castro, *J. Electron Spectrosc. Relat. Phenom.* 184, 384 (2011).

10:00am **AS+MC-MoM6 Angle-Resolved XPS Test Structures Fabricated In Situ by Argon Ion and Argon Cluster Ion Treatment**, *Peter Cumpson, A.J. Barlow, J.F. Portoles, N. Sano*, Newcastle University, UK

Nondestructive depth-profiling by inversion of Angle Resolved XPS spectra[1] has been a desire in the XPS community for a long time. The lack of reference specimens with known structures has been a severe handicap in

the development of the technique. Until now, reference materials with known depth-profiles have largely been confined to thin oxide layers on aluminium or silicon, and even these have uncertain carbon contamination layers. Progress has been made, though, with depth-profiling numerical methods[2] that need comparison with real known structures. It is difficult to fabricate structures with nanometre-scale variation in concentration with depth, and even more difficult to transport them without contamination (and the potentially damaging removal of such contamination).

We have developed protocols for the fabrication of two different samples, one organic and the other inorganic, with known depth-profiles *in situ* in XPS instruments;

Glancing-angle monatomic argon sputtered PEDOT:PSS, a common conducting polymer blend, and

Argon cluster-ion sputtered indium arsenide (InAs), a compound semiconductor

Indium arsenide and PEDOT:PSS are both widely-available, almost atomically flat and sufficiently electrically conductive to ensure no sample charging occurs. Glancing angle monatomic sputtering of PEDOT:PSS leaves a PEDOT enhanced region at the surface, the spatial parameters of which depend only on sputter ion conditions under direct experimental control. Recently we have demonstrated the unexpected result that argon gas-cluster sputtering of InAs results in a thin, coherent metallic indium layer at the surface[3], the basis for InAs reference material structure.

The ill-posed nature of the inversion of ARXPS data means it is sensitive to small experimental uncertainties. We apply three different ARXPS algorithms, including regularization, to the data from these *in situ* reference structures. This gives a set of reference data that will allow comparison with results from any XPS work following the same preparation protocol. This should greatly improve confidence in the results of ARXPS depth-profiling.

[1] P J Cumpson, Angle-resolved XPS and AES: depth-resolution limits and a general comparison of properties of depth-profile reconstruction methods, *J Electron Spectrosc. and Rel. Phenom.* 73 (1995) 25-52.

[2] R W Paynter, Regularization methods for the extraction of depth profiles from simulated ARXPS data derived from overlayer/substrate models, *J Electron Spectrosc. and Rel. Phenom.* 184 (2012) 569–582.

[3] A J Barlow and P J Cumpson, Observed damage during Argon gas cluster depth profiles of compound semiconductors, submitted to *J Appl. Phys.*

10:40am **AS+MC-MoM8 Metrology for Surface Chemical Analysis: Active Parties, Status and Challenges**, *Wolfgang Unger*, BAM Federal Institute for Materials Research and Testing, Germany

The International Bureau of Weights and Measures (BIPM) defines metrology, i.e. the *Art of Measurement*, as "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology." Besides the establishment of full uncertainty budgets traceability is another aspect of metrology.

Surface chemical analysis is a much younger discipline in comparison to other branches in analytical chemistry as, e.g., electro-chemistry, inorganic and gas analysis and lots of work has to be done to make XPS, AES and SIMS based quantitative analysis a metrological one. Looking to the analytical methods established in surface chemical analysis we may differentiate classes:

1. Primary methods measuring amount of substance as [atoms/cm², ...]
2. Empirical methods measuring amount of substance after calibration as fractions of a nano scaled surface layer
3. Primary and empirical methods measuring amount of substance expressed as the thickness of a thin film [nm]

In most cases we are using empirical methods when XPS, AES and SIMS are applied to deliver quantitative data. It follows also from that list that, principally, traceability to the mol or the meter can be established.

Relevant initiatives to metrologically underpin surface chemical analysis have been launched under the umbrella of the Surface Analysis Working Group at CCQM/BIPM where the National Metrology Institutes are running world-wide inter-laboratory comparisons. In Europe we have the European Metrology Research Program (EMRP) where a number of projects directly address issues of surface chemical analysis and most often also by individual websites. Another aspect is that there is a strong impact of metrology in surface chemical analysis on standardization in ISO TC 201 and 202. For example, ISO 14701 has been prepared using outcome of a huge key comparison organized under CCQM/BIPM.

The talk will present some basics of metrology in surface chemical analysis, results of successful key comparisons organized under CCQM/BIPM and a survey on the main scientific challenges to be addressed in quantitative surface chemical analysis in the next future.

11:00am **AS+MC-MoM9 Local Crystallography: Phases, Symmetries, and Defects from Bottom Up**, *A. Belianinov, Q. He, A. Borisevich, S. Jesse, Sergei Kalinin*, Oak Ridge National Laboratory

Progress in high-resolution real space imaging techniques such as (Scanning) Transmission Electron Microscopy (STEM) and Scanning Tunneling Microscopy (STM) has allowed high veracity, direct imaging of atomic columns (STEM) and surface atomic structures. While the data acquisition platforms are continuously evolving, the basic data processing principle - analysis of structure factor, or equivalently two point correlation function averaged over probing volume - remained invariant since the early days of Braggs. We propose an approach based on the multivariate statistical analysis of the coordination spheres of individual atoms to reveal preferential structures and symmetries. The underlying mechanism is that for each atom, *i*, laying on the lattice site with indices (*l, m*), we construct a near coordination sphere as a vector $\mathbf{N}_i = (x_1, \dots, x_8)$, where (*x_j, y_{j+}*) is the radius-vector to *j*/2-th nearest neighbor. Once the set of \mathbf{N}_i vectors is assembled, its statistical properties are analyzed through cluster analysis and various multivariate methods to reveal and extract regions of symmetry, distortions, different phases, boundaries, defects, etc. Results are presented on various model and real material systems including La_{0.7}Sr_{0.3}MnO₃, BiFeO₃, LaCoO₃ and discussed in light of physical parameter extraction.

Acknowledgement:

Research for (AB, QH, AB, SJ, SVK) was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

11:20am **AS+MC-MoM10 Chemical Warfare Agent Surface Adsorption: Hydrogen Bonding of Sarin and Soman to Amorphous Silica**, *Erin Durke, W.O. Gordon*, Edgewood Chemical Biological Center, *A.R. Wilmsmeyer*, Augustana College, *D. Troya, J.R. Morris*, Virginia Tech

Sarin and soman are warfare nerve agents that represent some of the most toxic compounds ever synthesized. The extreme risk in handling such molecules has, until now, precluded detailed research into the surface chemistry of agents. We have developed a surface science approach to explore the fundamental nature of hydrogen bonding forces between these agents and a hydroxylated surface. Sarin and soman are deposited via a directional doser onto an amorphous silica surface and characterized by reflection-absorption infrared spectroscopy (RAIRS) in an ultra-high vacuum (UHV) chamber. Once the chemical agent coverage reached monolayer values, temperature programmed desorption is performed to determine the binding energy. Changes in the OH region of the IR spectra are monitored in real time with RAIRS, and the degree of shift in the H-bonded OH peak shows a linear relationship with the strength of the interaction between agent and silica surface. Infrared spectroscopy revealed that both agents adsorb to amorphous silica through the formation of surprisingly strong hydrogen-bonding interactions with primarily isolated silanol groups (SiOH). Comparisons with previous theoretical results reveal that this bonding occurs almost exclusively through the phosphoryl oxygen (P=O) of the agent. Temperature-programmed desorption experiments determined that the activation energy for hydrogen bond rupture and desorption of sarin and soman was 50 ± 2 kJ/mol and 52 ± 2 kJ/mol, respectively. X-ray photoelectron spectroscopy (XPS) is also used to confirm molecular desorption of the agents from the silica substrate. Together with results from previous studies involving other phosphoryl-containing molecules, we have constructed a detailed understanding of the structure-function relationship for nerve agent hydrogen bonding at the gas-surface interface.

11:40am **AS+MC-MoM11 The Shake-up Satellites in the Fe 2p Core Level X-ray Photoelectron Spectra Analyzed with the Double Lorentzian Line Shape**, *M. Bravo-Sanchez*, CINVESTAV-Queretaro, Mexico, *J.A. Huerta-Ruelas*, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Mexico, *A. Herrera-Gomez*, CINVESTAV-Queretaro, Mexico, *M.O. Vazquez-Lepe*, Universidad de Guadalajara, Mexico, *F. Espinosa-Magaña*, CIMAV-Unidad Chihuahua, Mexico

Within the transition metal oxides, Fe oxides are among the most technologically relevant. Surfaces analysis through techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in the development of new applications. Despite that a considerable effort has been made on Fe oxides with XPS, many questions are still unanswered mainly due to the lack of a simple and standardized method to adequately model the spectrum of the Fe 2p core level. Complex characteristics such as a steeply background, shake-up satellites, and an asymmetrical line-shape, have been the principal obstacle to obtain accurate areas for proper quantification. In this work, this problem has been confronted by employing the SVSC background [1] and the double Lorentzian line shape [2]. The

latter has many advantages over the traditionally employed Doniach-Sunjić line shape, since it is integrable and, then, suitable for quantitative studies.

With this combination of methods it has been possible to closely model the entire Fe $2p$ spectra (including both the $3/2$ and $1/2$ branches), which implied accounting for the shake-up satellite already known and the inclusion of a second satellite rarely reported in the literature. A proper determination of areas for accurate quantification of composition and thickness has been achieved taking into account this second satellite located around 725 eV (binding energy), hidden under the $1/2$ branch of the main oxide peak. The inclusion of this second signal, together with the already known satellite, improves notably the quantitative analysis of the Fe oxides spectra. The position of the satellites shows a clear dependence on the oxide thickness. Thickness assessment has been confirmed with high-resolution transmission electron microscopy.

[1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. *Journal of Electron Spectroscopy and Related Phenomena* (in press) DOI 10.1002/sia.5453.

[2] A. Herrera-Gomez. "A double Lorentzian shape for asymmetric photoelectron peaks." Internal Report. Cinvestav-Querétaro.(2011). <http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf>

Authors Index

Bold page numbers indicate the presenter

— B —

Barlow, A.J.: AS+MC-MoM6, 1
Belianinov, A.: AS+MC-MoM9, 2
Borisevich, A.,: AS+MC-MoM9, 2
Bravo-Sanchez, M.: AS+MC-MoM11, **2**
Bushell, A.: AS+MC-MoM1, 1

— C —

Ceballos-Sanchez, O.: AS+MC-MoM2, 1
Cumpson, P.J.: AS+MC-MoM6, **1**

— D —

Durke, E.M.: AS+MC-MoM10, **2**

— E —

Espinosa-Magaña, F.: AS+MC-MoM11, 2

— G —

Gordon, W.O.: AS+MC-MoM10, 2

— H —

He, Q.: AS+MC-MoM9, 2

Herrera-Gomez, A.: AS+MC-MoM11, 2; AS+MC-MoM2, **1**

Huerta-Ruelas, J.A.: AS+MC-MoM11, 2

— J —

Jablonski, A.: AS+MC-MoM5, 1
Jesse, S.: AS+MC-MoM9, 2

— K —

Kalinin, S.V.: AS+MC-MoM9, **2**

— M —

Mack, P.: AS+MC-MoM1, 1
Mani-Gonzalez, P.G.: AS+MC-MoM2, 1
Morris, J.R.: AS+MC-MoM10, 2

— N —

Nunney, T.S.: AS+MC-MoM1, 1

— P —

Portoles, J.F.: AS+MC-MoM6, 1
Powell, C.J.: AS+MC-MoM5, **1**

— S —

Sano, N.: AS+MC-MoM6, 1

— T —

Tanuma, S.: AS+MC-MoM5, 1
Troya, D.: AS+MC-MoM10, 2

— U —

Unger, W.: AS+MC-MoM8, **2**

— V —

Vazquez-Lepe, M.O.: AS+MC-MoM11, 2;
AS+MC-MoM2, 1

— W —

Werner, W.S.M.: AS+MC-MoM3, **1**
Wilmsmeyer, A.R.: AS+MC-MoM10, 2
Wright, A.E.: AS+MC-MoM1, **1**

— Y —

Yeadon, A.: AS+MC-MoM1, 1