Tuesday Morning, October 31, 2017

Applied Surface Science Division
Room: 13 - Session AS+MI+SS-TuM

Quantitative Surface Analysis: Effective Quantitation Strategies
Moderators: Kateryna Artyushkova, University of New Mexico, Gregory L. Fisher, Physical Electronics

8:00am **AS+MI+SS-TuM1 Effective Attenuation Lengths for Different Quantitative Applications of XPS**, *A. Jablonski,* Institute of Physical Chemistry, Warsaw, Poland, ***Cedric Powell***, NIST

The effective attenuation length (EAL) is a convenient parameter for use in place of the inelastic mean free path (IMFP) to account for elastic scattering of signal photoelectrons in XPS. The most common EAL application is measuring the thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in laboratory XPS systems. EALs for this purpose can be obtained from a NIST database [1] and from empirical predictive equations [2]. In addition, EALs can be defined for other quantitative applications of XPS with laboratory XPS systems: (i) determination of thicknesses of overlayer films on planar substrates from changes of intensities of overlayer photoelectrons [3]; (ii) quantitative determination of surface composition by XPS [4]; and (iii) determination of shell thicknesses of core-shell nanoparticles [5]. Finally, EALs have been determined for measuring thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in XPS with linearly polarized X-rays with energies up to 10 keV [6]. These EALs will be compared to corresponding EALs for unpolarized X-rays [2,6]. The EAL is not a simple material parameter like the IMFP but depends on the defining equation for the particular application as well as on the experimental configuration.

1. NIST Electron Effective-Attenuation-Length Database, SRD 82, Version 1.3, 2011; https://www.nist.gov/srd/nist-standard-reference-database-82.

2. A. Jablonski and C. J. Powell, J. Electron Spectrosc. Relat. Phenom. 199, 27 (2015).

3. A. Jablonski, J. Electron Spectrosc. Relat. Phenom. 185, 498 (2012).

4. A. Jablonski and C. J. Powell (to be published).

5. C. J. Powell, W. S. M. Werner, A. G. Shard, and D. G. Castner, J. Phys. Chem. C 120, 22730 (2016).

6. A. Jablonski (to be published).

8:20am **AS+MI+SS-TuM2 Plumbing the Depths using the XPS Inelastic Background**, ***Alexander Shard***, *S.J. Spencer*, National Physical Laboratory, UK

A novel semi-empirical description of the intensity of inelastically scattered electrons in XPS is introduced. The functional form describes the background over the full energy range of an XPS survey spectrum and is not intended to be used as a background subtraction method. Therefore, it may be used even in the absence of elastic peaks in the spectrum. Samples of gold and silicon oxide coated with defined thicknesses of Irganox 1010 and a calibrated XPS spectrometer were used to generate reference data. These data were used to establish appropriately linked functions for substrate and overlayer background shapes as a function of overlayer thickness and the known relative intensities and energies of the pure materials. A common functional form could be found and appears to be of general utility, at least for organic overlayers. The description shows that the measurement of overlayer thicknesses well beyond the traditional XPS information depth is possible, for organic layers on gold this can be larger than 50 nm. In principle, the background shape of any substrate beneath an organic overlayer can be described and the thickness adjusted to match experimental data.

This description of XPS background shapes may be employed to rapidly confirm the chemistry and depth of substrate materials. Discrepancies with thicknesses established by traditional analyses of elastic peak intensities can be employed to measure defect densities in coatings. The use of background shape analysis should also be useful for measuring the overlayer thickness on topographic materials where traditional angle-resolved analysis is not appropriate. Furthermore, these descriptions should be useful for new developments in XPS, such as nanoparticle shell measurement, high energy XPS and near-ambient pressure XPS.

8:40am **AS+MI+SS-TuM3 Quantitative Organic Depth Profiling and 3D Imaging using Secondary Ion Mass Spectrometry**, ***Rasmus Havelund***, National Physical Laboratory, UK **INVITED**

The development of gas cluster ion beams has transformed the ability for depth profiling of organic materials using secondary ion mass spectrometry (SIMS). The technique now permits molecular information to be obtained with excellent depth resolution to depths of several µm. This type of analysis is highly valuable across a range of applications but quantitative analysis continues to be a major challenge.

Carefully prepared organic reference multi-layers have in a number of studies been used to measure gas cluster ion sputtering yields[1,2], depth resolutions[1,2], and, recently, the matrix effect in binary molecular mixtures[3]. These parameters are important in any attempt to achieve quantification. Here, the ability to accurately measure the thickness of organic layers and the depth of interfaces is evaluated using such organic reference multi-layers. The depth of interfaces is needed for materials or devices consisting of distinct layers of pure single materials where a measurement of the thicknesses of the layers provides, quantitatively, the amount of substance in the layers. In sputter depth profiling, the thickness of a layer will be reflected in the primary ion dose required to remove the layer, and in the integrated characteristic secondary ion signal intensity through that layer. A detailed analysis of the critical role of the matrix effect on these parameters is provided, and the prospects for measuring compositions in mixed materials are discussed based on results from three different sample systems. This provides useful information for the development of quantification strategies.

[1] Niehuis et al., Surface and Interface Analysis, 45, 158-162, 2013

[2] Shard et al., Analytical Chemistry, 84, 7865-73, 2012

[3] Shard et al., International Journal of Mass Spectrometry, 377, 599-609, 2015

9:20am **AS+MI+SS-TuM5 Coupling Effects on the Intensity and Background of the Cr 3*p* Photoemission Spectrum around the Cr 2*s* Threshold**, ***Alberto Herrera-Gomez,*** CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German,* Universidad de Sonora, *F.-S. Aguirre-Tostado,* CIMAV-Monterrey, *A. Dutoi,* University of the Pacific, *M.-O. Vazquez-Lepe,* Universidad de Guadalajara, *P. Pianetta,* Stanford University, *D. Nordlund,* Stanford Synchrotron Radiation Lightsource, *O. Cortazar-Martínez, L. Gomez-Muñoz,* CINVESTAV-Unidad Queretaro, Mexico, *A. Torrea-Ochoa*, CINVESTAV-Unidad Queretaro

By describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission, it is possible to understand many of the features found in XPS data ... as long as the photon energy is far away from the threshold of deeper core levels. For these cases, "the independent particle approximation, which had been thought to be applicable to atomic photoionization cross sections well above threshold, is clearly not applicable."[1,2] Even at energies away from deeper thresholds, quantification of the composition can be done only if we are also willing to employ empirical background subtraction methods such as the Shirley function to assess peak intensities. Through this method, employed in conjunction with others methods accounting for the background due to inelastic scattering (i.e., Tougaard background), it is possible to properly reproduce the experimental background [3] and assess the composition of surfaces. Of course, the intensity related to the background is ignored for composition calculations. Ignoring the background due to inelastic scattering is perfectly self-consistent because these electrons are effectively accounted by the Debye-Waller attenuation factor calculated from the inelastic mean free path. However, there is not any attenuation factor to account for the ignored Shirley electrons.

Through the study of the peak intensity of the Cr 3*p* peak with photon energies around the Cr 2*s* threshold, we found that these two issues, 1) channeling effects on the peak intensity and 2) the need to ignore the Shirley electrons for composition calculations, are, in fact, related. The behavior of the Cr 3*p* background strongly suggest coupling between the 3*p* and the valence states. These coupling most exist for a brief time after photon absorption, and the observed photoelectrons should actually come from one of these coupled states. That is, "describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission" is not the complete paradigm for photoemission.

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

[2] W. Drube, T.M. Grehk, S. Thieß, G.B. Pradhan, H.R. Varma, P.C. Deshmukh, S.T. Manson, Pronounced effects of interchannel coupling in

high-energy photoionization, 46 (2013). doi:10.1088/0953-4075/46/24/245006.

[3] 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.

9:40am **AS+MI+SS-TuM6 Using Main Peak Intensities for XPS Quantitation: Strengths, Weaknesses, Issues**, ***B. Vincent Crist,*** XPS International LLC, *C.R. Brundle*, C. R. Brundle and Associates

It is common, in the practical world, to use the most intense XPS peaks from survey spectra, in combination with instrument software RSF's, for atom percent quantitation. The advantage is obvious: time saved. Occasionally, peak overlaps force the use of a secondary peak plus a ratio of RSF's. The origin of that ratio is usually based on theoretical cross-sections, σ (1), corrected for transmission function, T, and escape depth, λ.

Using clean elemental surfaces the validity of using relative σ's for peaks in the spectrum was tested. Some large discrepancies were found. The same occurred for some crystal materials and bulk polymers. Two possible causes are errors in σ's, or variations in intensity losses to satellites, invalidating the use of main peak intensities plus σ values (σ includes intensity from all final states). σ values should be good to better than 10% error (1). Intensity losses can vary with core level, but there are examples here where this does not seem to be the problem.

Suppliers' RSF's come either from theoretical σ's (1), or from empirical standards (2) where only main peaks are included. Except for 1st row elements there are significant discrepancies (>30%) between the approaches. We discuss possible reasons and note:

(a) the suppliers' empirical standard based RSF's all seem to be derived from the data of Wagner, et al. (2). That Herculean study included results from other studies on a range of poorly characterized instruments and samples whose surface compositions might be suspect.

(b) The discrepancies cannot be explained by the lack of inclusion of satellite intensities for the standards approach, as any correction generally worsens agreement.

We conclude it is time for a reexamination of the standards approach with modern instruments and better controlled samples. It is now possible to theoretically estimate the fraction of total intensity lost to satellites (3) and so to establish what fraction of σ should be used when relying on main peak intensities.

1 J. H. Scofield, J. Elec. Spec. 8, 129 (1976)

2 C. D. Wagner, et al, Surface Interface Analysis, 3, 211, (1981)

3 P. S. Baguset al., J. Chem. Phys., in press (2017).

11:00am **AS+MI+SS-TuM10 XPS Spin-Orbit Splitting; Multiplet Splitting; Shake-up Losses: Implications for Determining Covalent Interactions and for Quantitative Analysis**, ***C. Richard Brundle,*** C.R Brundle & Associates, *P.S. Bagus*, University of North Texas

The "apparent" spin-orbit (S-O) splitting of metal cation core levels, observed by XPS for 3d transition metals, can vary with the ligand (anion) concerned, [1], even though true S-O splitting is an atomic property not depending on the atom's environment. However, multiplet splittings of the core-level XPS of 3d cations depend on 3d shell occupation [1-3], so variation in this can alter the apparent S-O splitting. Such variation should have a consequence on the relative positions of the no-loss S-O component peak positions (ie the XPS "apparent" S-O splitting), via the well-established Mann and Aberg Sum Rule. [4]. Here we establish the importance of a mechanism that also contributes to changes in the multiplet splitting, and so in the apparent S-O splitting. This mechanism is covalent mixing of metal cation and ligand orbitals (for example Ref [5]), which alters the exchange integrals between core and valence electrons.

For a closed 3d shell, eg Ti^{4+} there is no possibility of multiplet splitting, but an apparent discrepancy in the S-O component intensity ratio has been reported (1), and an explanation proposed involving different intensity losses to shake-up satellites from each component. Our calculations indicate identical intensity losses, however, and a reanalysis of the experimental data indicates that the correct intensity ratio can be recovered by simply including the lifetime broadening of the $2p_{1/2}$ component, which results in overlap between it and the $2p_{3/2}$ component.

We present theoretical evidence, bare cation and cluster calculations, which provide quantitative estimates of the importance of various mechanisms for the covalency and for changes in apparent S-O splitting. These calculations allow comparison of "apparent S-O splitting" to "true" S-O splitting, the latter defined as the difference of the relativistic orbital energies of the S-O split levels. Furthermore, they permit establishing the differing importance of covalency for different ligands, and thus a connection to the observation of differences in core-level XPS for different ligands [6]. These effects also have a consequence for quantitative analysis using the 2p and 3p cation XPS peaks, which will be discussed.

1. S. A. Chambers, in Hard X-Ray Photoelectron Spectroscopy (HAXPES), edited by J. C. Woicik (Springer, Heidelberg, 2016), Vol. 59, p. 341

2. R. P. Gupta and S. K. Sen, Phys. Rev. B , 71 (1974)

3. R. P. Gupta and S. K. Sen, Phys. Rev. B , 15 (1975)

4. R. Manne and T. Åberg, Chem. Phys. Lett. , 282 (1970)

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

6. M. Taguchi, T. Uozumi, and A. Kotani, J. Phys. Soc. Jpn. , 247 (1997)

11:20am **AS+MI+SS-TuM11 The Cu *2p* Photoemission Spectra from Mixed Oxidation States**, ***Jorge-Alejandro Torres-Ochoa,*** CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German,* Universidad de Sonora, Mexico, *M. Bravo-Sanchez,* Instituto Potosino de Investigación Científica y Tecnológica A.C, Mexico, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

Some X-ray photoelectron spectra have complicated structures that makes the peak fitting procedure difficult, especially with transition metals. Recent studies have shown the need to fit both branches of the *2p* spectra such as in Fe [1] and Co [2] This proved that modeling both branches concurrently is necessary to avoid errors such as area underestimation. In this report, copper films were obtained by sublimation in ultra-high vacuum ($5.5x10^{-8}$ torr) on Si(100) substrates. Immediately after deposition, the films were characterized by X-ray photoelectron spectroscopy using a monochromatic Al Kα source (hv=1486.7 eV). To study the initial stages of oxidation, the films were heat treated in an ultra-high purity oxygen atmosphere at 200 °C from 1 to 10 min.

From the photoemission spectrum, it was possible to observe three coexisting copper species. Using the Active Background Method,[3] an accurate fit was achieved for Cu *2p*. Both chemical species, Cu^{1+} (932.5 eV) and Cu^{2+} (933.5 eV), together with their satellites (Cu^{1+}: 946.5 eV, Cu^{2+}: 941.1 eV, and Cu^{2+}; 943.9 eV) were clearly identified.[4] The fit required two extra peaks at 934.7 eV and 942.4 eV. There is evidence that these peaks correspond to Cu^{3+}.

References

1. Bravo Sanchez, M., Huerta-Ruelas, J. A., Cabrera-German, D. & Herrera-Gomez, A. Composition assessment of ferric oxide by accurate peak fitting of the Fe 2p photoemission spectrum. *Surf. Interface Anal.* (2016). doi:10.1002/sia.6124

2. Cabrera-German, D., Gomez-Sosa, G. & Herrera-Gomez, A. Accurate peak fitting and subsequent quantitative composition analysis of the spectrum of Co 2p obtained with Al K α radiation: I: cobalt spinel. *Surf. Interface Anal.***48,** 252–256 (2016).

3. Herrera-Gomez, A., Bravo-Sanchez, M., Ceballos-Sanchez, O. & Vazquez-Lepe, M. O. Practical methods for background subtraction in photoemission spectra. *Surf. Interface Anal.***46,** 897–905 (2014).

4. Pauly, N., Tougaard, S. & Yubero, F. Determination of the Cu 2p primary excitation spectra for Cu, Cu 2O and CuO. *Surf. Sci.***620,** 17–22 (2014).

11:40am **AS+MI+SS-TuM12 Quantifying Valence Band Offsets at Metal\(Hf,Zr)O_2 Interfaces for Ferroelectric Devices**, ***Michael Brumbach**, S. Smith, M.D. Henry, J. Dickerson, D. Robinson Brown, J. Ihlefeld*, Sandia National Laboratories

The compatibility of HfO_2 deposition with current silicon microelectronic processing make it an appealing alternative to traditional ferroelectrics. A variety of applications, including Tunneling Electroresistance devices, can benefit from the switchable polarization of HfO_2-based thin films, first reported in 2011. In these devices the optimal band-alignment for electron transport is dependent on selection of top and bottom contact materials. In this work, the valence band offset of $(Hf,Zr)O_2$ with a number of metal contacts has been quantified by X-ray photoemission measurements. Coupled with experiment, simulations have been performed to identify the band offsets for successful device operation. Metal contacts investigated include Pt, Ni, Au, Al, Ta, and TaN. For some metal films there is the experimental consideration for the impact of air oxidation on the measured valence band offsets. In addition to characterizing films in a bottom-up approach, the metal layers were ion milled to thin the overlying metal and reveal the interfacial boundary. In such cases, the oxide was removed and valence band offset values were measured. The role of differential sputtering in mono-atomic and the application of gas cluster ion sputtering to alleviate differential sputtering will be discussed. Additional techniques including inverse photoemission, UV-photoemission, and Kelvin probe will be presented for further quantification of the valence band offsets.

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12:00pm **AS+MI+SS-TuM13 Quantitative Peak-Fitting Analysis of the Photoemission Spectra of Metallic Zinc and Zinc Oxide Films**, ***Dagoberto Cabrera-German***, Universidad de Sonora, Mexico, *G. Molar-Velazquez, G. Gómez-Sosa,* CINVESTAV-Unidad Queretaro, Mexico, *W. De la Cruz,* Universidad Nacional Autónoma de México, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The quantitative analysis of the X-ray photoelectron spectra of Zn and ZnO is a challenging task due to plasmon-loss features and small binding energy shifts that lead to inaccurate results on the assessment of the chemical state of mixed systems of metallic zinc and zinc oxide.[1] Additionally, the Zn 2*p* spectra hold a complex background that traditional background modeling methods are unable to reproduce accurately.

We have analyzed the Zn 2*p* and O 1*s* spectra of a metallic Zn film that has been subject to pressure and time controlled oxidations at high vacuum. Through the state-of-the-art peak-fitting methods[2–4] we have overcome the difficulties, as mentioned earlier, of performing a quantitative analysis of a metal and oxide system and we have also noted several interesting features of the Zn 2p spectrum.

We found that the assessed chemical composition for several oxygen exposures is $ZnO_{1.00\pm0.10}$, this suggests that the set of peak parameters employed to resolve the metallic and oxide photoemission signals, are accurate and can be applied in quantitative studies.

The main characteristic of the peak-fitting procedure is that close experimental data reproduction requires an individual assignment of Shirley backgrounds for each peak comprising the spectra. Therefore an accurate quantitative analysis can only be done employing the Shirley-Vegh-Salvi-Castle (SVSC) background under the active approach.[2–4]

Another feature is that the intensity of plasmon-peaks and their background are not accurately described by any existing energy loss (intrinsic and extrinsic) formalism. In fact, the modeling of their background trend requires the addition of an intense Shirley contribution, up to 10 times larger than the Shirley contribution of the main photoemission line. These are outstanding results that suggest that these plasmon-peaks are produced by a loss process that remains unaccounted.

[1] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, Appl. Surf. Sci. 257 (2010) 887–898.

[2] J. Végh, The analytical form of the Shirley-type background, J. Electron Spectros . Relat. Phenomena. 46 (1988) 411–417.

[3] A.M. Salvi, J.E. Castle, The intrinsic asymmetry of photoelectron peaks: dependence on chemical state and role in curve fitting., J. Electron Spectros . Relat. Phenomena. 95 (1998) 45–56.

[4] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. 46 (2014) 897–905.

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