

Applied Surface Science Division

Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-ThM

Quantitative Surface Analysis II

Moderators: Samantha Rosenberg, Lockheed Martin, Thierry Conard, IMEC, Belgium, Benjamen Reed, National Physical Laboratory, UK

8:00am **AS+CA+EL+EM+SE+SS+TF-ThM-1 OrbiSIMS: Signal, Noise and Transmission Are Three Sides of a Metrology Triangle**, G. Trindade, Y. Zhou, A. Eyres, National Physical Laboratory, UK; M. Keenan, Independent; Ian Gilmore, National Physical Laboratory, UK

In metrology, the science of measurement, a “metrology triangle” approach is used to provide a secure foundation. For example, the Quantum Metrology Triangle links Voltage, Resistance and Current through the Josephson Effect and the Quantum Hall Effect.

The OrbiSIMS¹, introduced in 2017, has become increasingly popular for biological and material sciences studies owing to its ability to give high confidence in molecular identification (mass resolving power > 240,000 and mass accuracy < 2 ppm) simultaneously with high confidence in localisation (micrometre scale spatially and nanoscale in depth). With a growing number of instruments internationally there is an increased need for metrology for reproducible measurements. We will show how Signal, Noise and Transmission form three sides of a metrology triangle that combine to enable better measurement. In a recent comprehensive study of the noise in an Orbitrap mass spectrometer, a probabilistic model was developed.² A region of the intensity scale is described by Poisson statistics allowing the scaling parameter, A, that relates ion current to the number of ions in the trap to be determined. A true signal intensity scale is then established which allows the useful yield of atoms in an implant layer to be measured. Through comparison with time-of-flight and magnetic sector instruments the fractional ion transmission is determined.³ We will discuss how Signal and Transmission combine to understand matrix effects in biological sample preparation and how understanding Signal and Noise are important for data analytical methods.

1. M. K. Passarelli. et al, I. S. Gilmore, Nat. Methods, 14(2017)12, 1175-1183.
2. M R. Keenan, G. F. Trindade, A. PirkI, C. L. Newell, K. Ayzikov, J. Zhang, L. Matjajic, H. Arlinghaus, A. Eyres, R. Havelund, J. Bunch, A. P. Gould, A. Makarov and Ian S. Gilmore, in preparation.
3. Y. Zhou, A. Franquet, V. Spampinato, G. F. Trindade, P. van der Heide, W. Vandervorst and I S Gilmore, in preparation.

8:20am **AS+CA+EL+EM+SE+SS+TF-ThM-2 Contribution of Imaging X-Ray Photoelectron Spectroscopy to Characterize Chrome Free Passivation Nano-Layer Deposited on Food-Packaging Tinplate: Composition and Chemical Environment**, E. Ros, Vincent Fernandez, CNRS, France; N. Fairley, CASAXPS, UK; B. Humbert, M. Caldes, CNRS, France

To protect metal from corrosion, passivation layer are widely used in food-packaging industry. Those Nano-metric protections create a thin oxide Nano-layer on the metal surface, making it less oxidisable. Common passivation are composed by chromium oxide[1], using hexavalent chromium as a reagent and reducing it. However, because of the toxicity of Cr(VI), European Union is gradually forbidding.Chromium Free Passivation Alternative is based on transitions metal oxides (Sn, Ti, Zr, Mn) and polymers. These samples present some roughness in few micron range observed by Atomic Force Microscopy.XPS Imaging were perform at different binding energy to allow extracting spectrum in each pixel over the eight (Mn 2p, O 1s, Sn 3d, Ti 2p,N 1s, C 1s, P 2s and Zr 3d) XPS core level process. This study show an anti-correlation between atomic concentration of Titanium and Tin Fig(1). We observe a ratio Sn oxide Sn metal homogeneous and independent of the Ti, Sn ratio More over using the vector method [2], [3] concurrently to height XPS core, we could extract two different chemical environments spectrum. The linear Least Square combination of these 2 spectrum allow us to model 131072 regions. To extract information form XPS data on heterogenous sample the combination of XPS imaging energy scan measurement with the vector method is a promising way. These results bring the useful information about different thin layer deposition steps. Imagerie XPS results are in agreement with Raman imagerie analysis

[1]R. Sandenbergh, M. Biermann, and T. von Moltke, ‘Surface Analytical Characterization of Chromium Passivation on Tinplate’, in *Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers*, P. Marcus and V. Maurice, Eds., Amsterdam: Elsevier Science, 2006, pp. 143–148. doi: 10.1016/B978-0-444-52224-5/50024-X.

[2]J. Baltrusaitis *et al.*, ‘Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model’, *Applied Surface Science*, vol. 326, pp. 151–161, Jan. 2015, doi: 10.1016/j.apsusc.2014.11.077.

[3]M. d’Halluin *et al.*, ‘Graphite-supported ultra-small copper nanoparticles – Preparation, characterization and catalysis applications’, *Carbon*, vol. 93, pp. 974–983, Nov. 2015, doi: 10.1016/j.carbon.2015.06.017.

8:40am **AS+CA+EL+EM+SE+SS+TF-ThM-3 Cryo-Xps for Surface Characterisation of Nanomedicines**, David Cant, National Physical Laboratory,, UK; Y. Pei, National Physical Laboratory, UK; A. Shchukarev, M. Ramstedt, University of Umea, Sweden; S. Marques, M. Segundo, University of Porto, Portugal; J. Parot, A. Molska, S. Borgos, SINTEF, Norway; C. Minelli, A. Shard, National Physical Laboratory, UK

Nanomedicines are an area of great interest for current and future pharmaceutical development. The use of nanoparticles to act as carriers for a therapeutic load has the potential to significantly improve medical outcomes, for example by allowing a therapeutic agent to circulate within the body for longer, or by allowing targeted delivery of a drug to a specific site. Such nanomedicines often rely on specific functional coatings to achieve their desired impact; for example the majority of nanomedicines currently available on the market utilise a poly-ethylene glycol (PEG) surface coating for its ‘stealth’ properties, helping nanomedicines evade the body’s clearance mechanisms. Accurate measurement of the surfaces of such nanomaterials is therefore of great importance, yet direct, quantitative surface chemistry measurements are not commonly available, and vacuum-based analysis methods such as XPS are unlikely to provide a representative measurement of the particles in their hydrated state.

Here we present to the best of our knowledge the first use of Cryo-XPS to provide direct, quantitative measurements of the surface chemistry of nanomedicines in a hydrated state. Two nanomedicine systems were measured: a drug-carrying polymer nanoparticle; and an mRNA loaded lipid nanoparticle. Both systems possessed a supposedly PEG-terminated surface, and were measured using XPS in both aqueous cryogenic state, and dry drop-cast onto a substrate. The results of these measurements clearly demonstrate that while the PEG surface cannot readily be observed in the dry state, the cryogenic measurements exhibit spectra that are consistent with the particle being measured in a hydrated condition.

9:00am **AS+CA+EL+EM+SE+SS+TF-ThM-4 Redox XPS as a Means to Address Some XPS Reproducibility Challenges**, Peter Cumpson, University of New South Wales, Australia

The challenge of better understanding of increasingly-complex specimens in surface analysis has been highlighted recently[1,2,3,4]. Especially at a time of high throughput XPS instruments and broadening of the (non-specialist) user community. An AVS survey conducted in 2018 found that 65% of those responding identified reproducibility as a significant issue [5].

There is an analogy to be made with some radically-different technologies. Machine Learning makes more sense of a moving image than a single snapshot, even if the snapshot were to come from a larger, better calibrated camera. Yet somehow we expect greater calibration precision, reference data and rigorous procedures to be the only route to reliable understanding of single spectra.

Generating a sequence of spectra from a progressively chemically-modified surface can remove many ambiguities that can otherwise cause misinterpretation. Such sequences thereby help with rapid understanding of the unmodified surface. On the theme of “Two is Better than One: Breaking Barriers with Coupled Phenomena” we present results from coupled stepwise oxidation/reduction of the surface and XPS to resolve such ambiguities for a wide range of materials and problems. Gas-phase oxidation agents are used to move through the redox states of a specimen in a controllable way, taking advantage of the logarithmic growth of oxide thickness. What is more, this oxidation is easy to implement in the entry-locks of modern XPS instruments through the use of vacuum ultraviolet light (VUV) and the *in situ* generation of ozone and gas-phase hydroxide free radicals. In the past there have been many studies of how particular materials react to ozone exposure at their surfaces, often employing XPS. Here we reverse this, and use ozone (and VUV) exposure to simplify the

interpretation of spectra from a wide range of unknown materials, we think for the first time.

[1] D R Baer et al, J. Vac. Sci. Technol. A 39, 021601 (2021); <https://doi.org/10.1116/6.0000873>

[2] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061204 (2020); <https://doi.org/10.1116/6.0000685>

[3] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061203 (2020) <https://doi.org/10.1116/6.0000377>

[4] D R Baer and M. H. Engelhard, Journal of Surface Analysis Vol. 26, No.2 (2019) pp. 94-95.

[5] D R Baer, J F Watts, A Herrera-Gomez, K J Gaskell, Surf Interface Anal. 2023; 1- 9. doi:10.1002/sia.7194

9:20am **AS+CA+EL+EM+SE+SS+TF-ThM-5 Sub-Nanometer Depth Profiling of Native Metal Oxide Layers Within Single Lab-XPS Spectra**, *Martin Wortmann*, N. Frese, Bielefeld University, Germany; *K. Viertel*, Bielefeld University of Applied Sciences and Arts, Germany; *D. Graulich*, M. Westphal, T. Kuschel, Bielefeld University, Germany

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here we propose a simple and accessible depth profiling approach for oxide layers with sub-nanometer depth resolution from single lab-XPS spectra. Metals and their oxides can be distinguished by a binding energy shift to quantify their distinct signal contributions. Analogous to the widely used Hill equation we utilize the known photoelectron's inelastic mean free path to calculate the characteristic oxide layer thickness. However, in contrast to the Hill equation we analyze not only one, but all orbital energies in the XPS spectrum to develop a model that accounts for a depth-resolved concentration profile at the oxide-metal interface. The proposed model not only improves the accuracy and reproducibility of earlier methods but also paves the way for a more holistic understanding of the XPS spectrum.

9:40am **AS+CA+EL+EM+SE+SS+TF-ThM-6 A Tag-and-Count Methodology Based on Atomic Layer Deposition (ALD) and Low Energy Ion Scattering (LEIS) for Quantifying the Number of Silanols on Fused Silica**, *Josh Pinder*, Brigham Young University

The concentration of surface silanols governs many of the properties of glass and fused silica surfaces including surface wetting, surface contamination rates, and thin film adhesion. Indeed, the concentration of surface silanols is impactful for diverse fields such as atomic layer deposition (ALD), chromatography, catalysis, and displays. Accordingly, various analytical and theoretical methods have been employed to determine the number of silanols on surfaces, including density functional theory, FTIR, thermogravimetric analysis, and temperature programmed desorption mass spectrometry. However, many of these methods are better applied to particulate materials than surfaces. In this presentation, we discuss a method for directly

measuring the concentrations of surface silanols on silica-containing surfaces via a tag-and-count methodology. This approach is based on tagging surface silanols by ALD via a single pulse of dimethylzinc or diethylzinc and then quantifying the number of tags (zinc atoms) using high

sensitivity-low energy ion scattering (HS-LEIS). Our method yielded the literature value for both fully hydroxylated fused silica and also fused silica that had been heated to 500, 700, and 900 C. We see this capability as enabling for all who work with glass, fused silica, and silicon wafers,

including for ALD.

11:00am **AS+CA+EL+EM+SE+SS+TF-ThM-10 ASSD Peter M. A. Sherwood Mid-Career Professional Awardee Talk: Providing Fundamental Mechanistic Insights Into Single-Site Catalytic Reactions**, *Jean-Sabin McEwen*¹, Washington State University

INVITED

The single atom limit achieves the ultimate degree of material efficiency for supported metal catalysts. To this end, the ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we provide new atomistic insights regarding the "44" Cu surface oxide through the integration of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) measurements, Synchrotron X-ray Diffraction measurements (SXRD), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) techniques. We also quantify the low-temperature CO oxidation kinetics on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure that arises when we further oxidize the "44" structure. Using STM, CO temperature programmed desorption (TPD), and DFT techniques, we determine that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings. Furthermore, we determine the state of the Pt single atoms before, during, and after reaction through a combination of theoretical and experimental techniques. We also correlate ambient pressure experiments, surface science measurements and first principles-based calculations to demonstrate that Pt/Cu(111) single-atom alloys (SAAs) oxidized with varying degrees of O₂ exposure can be reduced with H₂ with reasonable kinetics (hours). This is in contrast to oxidized pure Cu(111) where such reduction is very slow (days). We further contrast the catalytic properties of Rh/Cu(111) SAAs with varying degrees of O₂ exposure to the those of Pt/Cu(111) SAAs. Finally, we report the effects of a copper oxide thin film toward the segregation of noble metal single-atoms on Cu (111) using DFT.

11:40am **AS+CA+EL+EM+SE+SS+TF-ThM-12 Beyond the Physical Origin of the Shirley Background in Photoemission Spectra: Other Predictions of the Interchannel Coupling with Valence Band Losses Mechanism**, *Alberto Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The physical mechanism proposed in our 2017 paper about the origin of the Shirley background in photoemission spectra¹ es based on interchannel coupling² but with the important addition of energy losses in the valence band.³ Besides the Shirley background, it is possible to derive other predictions of the interchannel Coupling with Valence Band Losses mechanism (ICLM). Two of them are discussed in this paper: 1) the quantitative relation between Auger peaks and the Shirley background and 2) the conduction-band-like structure of the extended region of the Shirley background.

¹ A. Herrera-Gomez et al. Surface and Interface Analysis 50(2), 246–252 (2018).

² E.W.B. Dias et al. Phys Rev B 78(2), 4553–4556 (1997).

³

<http://www.qro.cinvestav.mx/~aherrera/reportesInternos/unknownOriginShirley.pdf>

12:00pm **AS+CA+EL+EM+SE+SS+TF-ThM-13 Aging of Hydrophilicity in a Nano-Textured SS316 Thin Film Fabricated by Magnetron Sputtering**, *Pakman Yiu*, Ming Chi University of Technology, Taiwan; *J. Chu*, *J. You*, National Taiwan University of Science and Technology, Taiwan

According to the structural zone model by J.A. Thronton[1], we may manipulate the surface morphology of a thin film by altering the deposition temperature and vacuum. Therefore in this study, we prepared a series of SS316 thin film by magnetron sputtering under different Argon working pressure. Resultant thin film possessed a pressure dependent nano-textured surface which was dependent on working pressure. Furthermore, we discovered that the textured surface was highly hydrophilic (water

¹ ASSD Peter Sherwood Award

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contact angle <15 degrees). The hydrophilicity could be attributed to the combinatorial contribution of surface roughness and capillary effect. However, we also discovered that the hydrophilicity aged with time, where after 21 days the surface turned hydrophobic with water contact angle >90 degrees. XPS studies on both as-deposited and 21-days stored sample films revealed that there was a Carbon-rich surface layer on the surface which grew with time. Interestingly when we tried to clean the surface with Argon atmospheric plasma, the hydrophilicity was almost fully restored. Results revealed that the aging of hydrophilicity may due to the fact that nano-surface texture gathers hydrocarbons in the atmosphere, which eventually formed an extra film that altered the surface wetting property. Understanding the aging mechanism and method of recovery may contribute to the development of a long-lasting hydrophilic surface, which is very useful in applications such as self-cleaning surface and medical apparatus[2,3]

[1] J.A. Thornton, *Ann. Rev. Mater. Sci.* 7 (1977) 239–260.

[2] A. Syafiq, B. Vengadaesvaran, A.K. Pandey, Nasrudin Abd. Rahim, J. *Nanomater.* 2018 (2018) 6412601.

[3] M. Xiao, Y.M. Chen, M.N. Biao, X.D. Zhang, B.C. Yang, *Mater. Biol. Appl.* 70 (2017) 1057–1070.

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