Applied Surface Science
Room: 204 - Session AS-TuM

Developments in Electron Spectroscopies for Non-Ideal Samples

Moderator: J.C. Woicik, National Institute of Standards and Technology (NIST), D.R. Baer, Pacific Northwest National Laboratory

8:00am **AS-TuM1 Chemical Analysis of Surfaces and Ultra-thin Films: At the Forefront of XPS Analytical Methods**, ***A. Rossi***, Università degli Studi di Cagliari and ETH Zurich, Italy **INVITED**

For decades it has been well known that the presence of layers of nanometer thickness can dramatically change the functional properties of a material, i.e. the corrosion resistance in aggressive environments, the wear and friction properties and more recently the leaching of minerals, the protein resistance and the biocompatibility of an implant.

Recent advances in x-ray photoelectron spectroscopy (XPS) enable examination of surface-chemical properties with far greater spatial resolution and accuracy than ever before, allowing the development of analytical strategies for understanding the mechanisms of surface-chemical reactions. These results offer unique possibilities for tailoring the surface properties of materials and for designing more sustainable and environmentally benign chemicals.

This presentation will focus on the most recent results: some of them are unpublished and others are already published within the framework of collaborations with other groups.

From XP-spectra to thickness and composition of nanostructured materials and of solutions

One of the unique characteristics of XPS is its capability of providing information on the thickness and composition of materials with layers of nanometer thickness in a non-destructive way. In this presentation, I will discuss the results of the research performed with the aim of understanding films only a few nanometers thick. Topics are the chemical-state identification of different elements and the ordering of molecules within the films. Examples from our research on multi-component alloys, including 'real systems' such as steels, self-assembled monolayers (SAM) and organically functionalized bio-surfaces will be presented. The mathematical algorithms will be critically evaluated for practical applications.

Very recent angular-resolved XPS results of tetraethyl-ammonium bromide (TEABr) in polyethylene glycol (PEG) 200 are shown to demonstrate the spatial distribution at the vacuum-solution interface.

Imaging XPS: the importance of visualization of chemical information

Imaging XPS is one of the most powerful tools that are available nowadays for investigating the surface of heterogeneous samples. Chemical maps recorded on steel samples after tribological testing at pressures of some GPa and up to 150°C are processed with principal component analysis, allowing the identification of polyphosphates with different chain lengths and the reconstruction of compositional and thickness maps. The relevance of these results for the development of new, more environmentally compatible and sustainable anti-wear and friction modifier additives will be discussed.

8:40am **AS-TuM3 Sample-Morphology Effects on XPS Peak Intensities: Estimation of Detection Limits**, ***C.J. Powell***, National Institute of Standards and Technology (NIST), *W.S.M. Werner, W. Smekal*, Technical University of Vienna, Austria

It has long been known that variations in sample morphology can have drastic effects on photoelectron intensities in XPS and thus on the results of quantitative analyses [1]. While detection limits for minor species in homogeneous samples have often been estimated to be between 0.1 and 1 atomic percent, no estimates are generally available for inhomogeneous samples. In general, detection limits depend on the detectability of a particular peak (which depends on the peak-detection method, the measurement statistics, peak identification, and interpretation in relation to the known or assumed sample morphology).

We have used the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [2,3] to estimate detection limits for buried thin films. Test simulations have been performed for thin W films of varying thicknesses buried at varying depths in a Ru matrix. For these simulations, the X-rays were incident normally on the sample and the photoelectrons were detected at an emission angle of 55° with respect to the sample normal. We initially established that the W $4d_{5/2}$ peak intensity would likely be detectable in a $RuW_{0.001}$ alloy (for which the ratio of the W $4d_{5/2}$ peak intensity to the Ru $3d_{5/2}$ peak intensity was 1.25×10^{-3}). Simulations were then performed with a thin W film on a Ru substrate and for thin W films at selected depths in the Ru matrix. In each case, we varied the W film thickness to obtain the same W $4d_{5/2}$ peak intensity (within 1%) as for the $RuW_{0.001}$ alloy. We find that the defined detection limit in this example varies by over three orders of magnitude for a thin W surface film to a W film buried to depths up to six times the inelastic mean free path.

[1] S. Tougaard, J. Vac. Sci. Technol. A 14, 1415 (1996).

[2] NIST SRD 100, Version 1.3 (2011); http://www.nist.gov/srd/nist100.cfm.

[3] W. Smekal, W. S. M. Werner, and C. J. Powell, Surf. Interface Anal. 37, 1059 (2005).

9:00am **AS-TuM4 The Active-Background Method in XPS Data Peak-fitting**, ***A. Herrera-Gomez***, CINVESTAV-Queretaro, Mexico

Quantifying the intensity of peaks in x-ray photoelectron spectroscopy (XPS) data requires the proper modeling of the background signal. This is traditionally accomplished by first assessing the background intensity and then peak-fitting the backgroundless spectrum. One of the main disadvantages of the traditional or static method is that it usually requires forcing the background to pass through two user-defined points, one at each side of the spectrum. In contrast, with the active-background method the intensity and shape of the background are defined during the peak-fitting process. Other advantages of the active method are the following:

• The area of the peaks is frequently underestimated when the static method is employed. This is because the operator typically cannot guarantee that there is no appreciable contribution to the signal at the two chosen points; instead, the operator has to assume it.[1].

• The relative contributions of the Gaussian and Lorentzian widths to the FWHM of the peaks are dependent on the fitting energy range when the static method is employed.

• The traditional (static) iterative Shirley-Sherwood background algorithm might fail for some types of spectra. This is not the case for the Shirley Sherwood background when the active method is employed. Another issue is that it takes longer to converge, that is, more iterations are required with the static than with the active method.

• The active treatment allows for simultaneously applying a combination of background types.

• When the background is subtracted before peak-fitting, the Poisson-character of the data is no longer applicable, so the uncertainty of the peak parameters cannot be calculated employing the covariant matrix method.

• The operator might stop thinking about about the background once it has been subtracted, which can lead to errors in the static method. In the active method, the changing role of the background is accounted for as the operator considers other options during peak-fitting.

• Last, but not least, the active method always provides better fits than the static method.

The importance of implementing the active background had been discussed in other reports.[2,3] In this talk some practical examples of the application of the active-background method are fully discussed.

[1] J. Muñoz-Flores, A. Herrera-Gomez. "Underestimation of the peak areas for the static and active background methods in XPS data peak-fitting." To be submitted.

[2] A.M. Salvi and J.E. Castle. J. Elec. Spec. Rel. Phen. 95 (1988) 45.

[3] J. Vegh. J. Elec. Spec. Rel. Phen. 46 (1988) 411.

9:20am **AS-TuM5 Angle-Resolved XPS of Compound Semiconductors: A Straightforward Route beyond the "Relative Depth" Plot**, ***A. Barlow***, *P. Cumpson*, NEXUS, Newcastle University, UK

There is an ever-present need to characterise surfaces and interfaces with increasing sensitivity and precision. One frequently-used tool to do this is the "Relative Depth Plot" (RDP) that can be derived very easily from Angle-Resolved XPS spectra. Despite the name, this does *not* plot relative depth, but relative *attenuation* of the signal electrons. For peaks widely-separated in energy this will lead to errors, so that even the order of layers, not just their depth, is incorrect. This may be obvious to XPS practitioners, but to those collaborating with them, or those new to XPS such as many of our clients, the name "Relative Depth Plot" plot can be extremely misleading.

Compound semiconductors are a class of specimen that is ideal for illustrating these issues. Available in good quality they have known

compositions, low roughness and have a high degree of homogeneity, so that the composition as a function of depth is well-known. We have analysed a wide range of compound semiconductors including ZnSe, InAs, InSb, GaAs, GaP and CdTe using our parallel acquisition Angle-Resolved XPS instrument, using an argon gas cluster ion beam (GCIB) to clean these surfaces without damage. We present the results of applying RDP, Stratification[1], and some variants of these methods.

We develop a very simple correction factor that greatly improves (but does not completely eliminate) the RDP problem and which can be applied automatically. This is particularly valuable for many semiconductor materials that are of industrial significance. Understanding the nature of the surface of an active material, or the interface between two active materials, such as in a junction or at the surface of a photo-active sensor, is crucial for novel device development and advancement. It is even more important to interpret Angle-Resolved XPS spectra correctly in cases where layer order is genuinely unknown, as is often the case in biological problems, for example.

Finally, some investigations of sputter depth profiling of these materials using novel ion beam technology, argon gas clusters, will be discussed.

[1] M P Seah et al, Surf and Interface Anal. 21 (1994) 336–341

9:40am **AS-TuM6 The Effect of Electronic Relaxation on the First-Principles Prediction of XPS Spectra**, ***K. Artyushkova**, S. Akbir,* University of New Mexico*, B. Kiefer*, New Mexico State University

Catalysts find use in many scientific and engineering applications. One of the recurring themes in this context is the quest for the design of suitable catalysts with improved performance. A prerequisite for the rational design is the identification of the nature of the catalytic site(s). XPS is a widely used experimental technique for this purpose. However, the unique identification of structural motifs from XPS observations remains challenging. First-principles computations can provide the missing link by predicting core-level shifts for candidate structural motifs of the catalytic sites. Here we focus on carbon supported TM-Nx (TM=Fe, Co) electrocatalysts, a class of ORR electrocatalysts that continues to attract significant attention for applications in fuel cells. Using density-functional-theory (DFT) we predict the Fe2p and N1s core level shifts for carbon embedded candidate TM-Nx (TM=Fe, Co; x=1-4) motifs. In particular we will discuss single versus multi-electron excitations, the effect of electronic relaxation in the final state approximation and provide a comparison our experimental observations.

10:40am **AS-TuM9 XPS for Characterisation of Optical and Electronic Devices under Operation**, ***S. Suzer***, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is performed to investigate a number of optical and electronic devices under operation. The main objective of the technique is to trace chemical and location specified surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of single and multi p-n junctions made out of Si. GaN and Graphene have been investigated under light illumination and/or under forward as well as reverse bias. The main advantage of the technique is its ability to assess element-specific surface electrical potentials of devices under operation based on the energy deviation of core level peaks in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to the energy of the illuminating source under operation is also shown to be capable of detecting, locating, and identifying the chemical nature of structural and other types of defects.

11:00am **AS-TuM10 Practical Auger Spectroscopy**, *M.D. Johnson,* Hewlett Packard*, D.F. Paul,* Physical Electronics Inc.*,* ***W.F. Stickle***, Hewlett Packard*, J.F. Moulder*, Physical Electronics Inc.

Auger spectroscopy is a mainstay in many analytical laboratories where high spatial resolution and compositional analysis are necessary for problem solving. Two related questions often come up during an analysis. The first question has to do with quantification and is there a way to sort out the different chemistries observed on a sample, either spatially in x or y or as a function of depth. The second analytical question has to do with detection of trace amounts of a material especially in the presence of peak overlap. Various approaches to these practical questions can be used such refining relative sensitivity factors and the application of numerical methods. Further, the use of high spectral resolution data may increase the ability to detect trace amounts of a material in a complex matrix as well as to increase the detection limits of the analysis. These questions are explored using practical systems of silicon, silicon dioxide, silicon nitride and silicon carbide where the Si KLL peaks shift and change lines shape. Practical aspects of detection limits are illustrated in the examination of trace amounts of silicon and/or hafnium in a tantalum oxide matrix where there is overlap between the Si KLL, Ta MNN series and the Hf MNN series Auger transitions.

11:20am **AS-TuM11 Angle-resolved Photoemission from Curved Surfaces**, ***J.E. Ortega**,* Universidad del País Vasco, Spain*, F.M. Schiller, J. Lobo-Checa,* CSIC, Spain*, A. Mugarza*, Institut Catala de Nanotecnologia, Spain

Surfaces that are vicinal to high symmetry directions have frequently demonstrated their enormous potential for surface science research and applications. Vicinal surfaces characterized by arrays of atomic steps exhibit distinct chemical and physical properties, but they are also useful as templates for nanostructure growth, and, more generally, to transmit uniaxial and/or chiral symmetry to epitaxial layers. In this context, curved surfaces with a smooth variation of the vicinal angle, i.e., a tunable step lattice constant, allow a straightforward and rational investigation of all physical-chemical phenomena related to the presence of atomic steps. In particular, we have used curved noble metal surfaces to investigate the electron scattering problem at atomic steps on bare surfaces, monolayers and thin films, using Angle-resolved photoemission and micron-size light spots that are scanned over the surface. I will discuss through a number of cases the limits and advantages of using such curved surface approach for ARPES studies.

11:40am **AS-TuM12 Uncovering the Mechanism of Bioleaching of Enargite by XPS**, ***M. Fantauzzi**, B. Elsener, G. Rossi, A. Rossi*, Università degli Studi di Cagliari, Italy

Sulfide minerals biooxidation processes (oxidation mediated by microorganisms) are particularly suitable for gold recovery from low-grade ores and are more environmentally friendly compared to conventional physicochemical mineral beneficiation processes. Oxidative dissolution mediated by microorganisms besides being of economic interest is environmentally significant since the latter usually occur in AMD (Acid Mine Drainage) and play a decisive role in the release of toxic elements such as Arsenic into the environment. According to the integral model for bioleaching [1], Fe (III) and H^+ ions control sulfides dissolution and the role of bacteria is to catalyze Fe (III) and H^+ regeneration and to concentrate those oxidants at the mineral surfaces by extra-cellular polymeric substances (EPS). EPS is produced by the living bacteria and forms kind of a bridge between the cell and the mineral surface. As the EPS layer is able to complex iron (III) ions into glucuronic acid-iron complexes, the actual concentration of iron (III) ions on the mineral surface may be higher than their concentration in the surrounding solution. This work aims to provide surface analytical and electrochemical evidences of the dissolution mechanism of enargite (Cu_3AsS_4). All experiments were carried out in presence of a strain of *Acidithiobacillus ferrooxidans* adapted to arsenic and of iron ranging from 10^{-5} M to 10^{-3} M at pH 2. The electrochemical potential was found to increase explaining the higher dissolution rate observed in the presence of bacteria. The enargite solubility was strongly enhanced by *A. ferrooxidans*: solution analyses showed that Cu and As dissolved stoichiometrically with a dissolution rate of about 3 - 5 times higher compared to the abiotic control.

The XPS C1s, O1s, N1s and P2p regions acquired on bacterial cells and on bioleached mineral grains were processed so that the surface composition of the EPS layer was obtained. The fraction of proteins, hydrocarbon and polysaccharides of the EPS was estimated and monitored for a period of time up to 157 days. Also the iron signal initially absent was observed after bioleaching.

The average thickness of the EPS layer at the mineral surfaces, as well as the protein content, increases with bioleaching time from 1 nm (after 44 days) to 2.5 nm (after 157 days) whereas the hydrocarbons and polysaccharides amount decrease with leaching time. These results are thus demonstrating the role of EPS in the sulphide dissolution and substantiate the model for bioleaching.

1. W. Sand, T. Gehrke, P. Josza, A. Schipper, Hydrometallurgy 59 (2001) 159 - 175

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