Applied Surface Science Division
Room A211 - Session AS+BI+CA+LS-TuA
Beyond Traditional Surface Analysis

Moderators: Michaeleen Pacholski, The Dow Chemical Company, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **AS+BI+CA+LS-TuA-1 Nanotechnology as a Driver for Going Beyond Traditional Surface Analysis***, **Olivier Renault**,* CEA-LETI, France **INVITED**

In the last 10 years, the progress of analytical methods has been more and more strongly connected to the pressing needs from materials and processing developments in the nanoelectronics industry. The field of materials analysis is now expanding as more and more complementary information are needed to tailor new materials for particular applications. Time-consuming techniques in the past (e.g, ARPES) are now accessible with increasing throughput, whereas the reliability of others, such as depth profiling, is improving. Finally, techniques like HAXPES implemented in the past only at synchrotron facilities, are now entering into laboratories.

In this talk I will illustrate by a series of examples in the field of device technology this evolution of surface analysis getting beyond traditional methods, driven by technological developments.

3:00pm **AS+BI+CA+LS-TuA-3 Core Levels Sub-shell Photo-ionization Cross-sections of Au, Ag, Cu in the Hard X-ray Photon Energy Range of 7-26 keV***, **Germán Rafael Castro**, J Rubio Zuazo,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Hard X-ray Photo-electron spectroscopy (HAXPES)[1] has been developed in the last 10-15 years as a unique tool for retrieving accurate non-destructive[2] compositional and electronic bulk property of materials in the tens of nano-meters depth-scale with nano-meter resolution. Furthermore, the ability to tune the excitation energy in the hard X-ray regime enables tuning the sampling depth, i.e. depth profile analysis, but also enables the discrimination between bulk and surface effects, especially if combined with variable incident and exit angle.

However, an important drawback is the lack of knowledge of the photo-ionization cross-section at the HAXPES photon energy and in special for now accessible deeper core levels. Recently theoretical data has been reported [6] concerning the photo-ionization cross sections and parameters of the photo-electron angular distribution for atomic subshells but for binding energies lower than 1.5 keV of all elements with 1≤ Z ≤ 100 in the photon energy range 1.5–10 keV. Unfortunately, these calculations do not contain information for deep orbitals accessible in HAXPES, even more there are scarce experimental results reported for both depth core levels and hard x-ray excitation energies.[3,4]

In the present work we will show the experimentally obtained relative sub-shell photo-ionization cross sections for 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d core levels of gold (Au), 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d core levels of silver (Ag) and 1s, 2s, 2p, 3s, 3p, 3d core levels of Cooper (Cu) in the X-ray photon energy range of 7–26 keV. In the case of Au, cross sections have been corrected with experimental obtained angular anisotropy parameter. A comparison with theoretical sub-shell photo-ionization cross sections, and angular anisotropy photo-inionization parameters [5,6] will be also presented.

References

1. J. Rubio-Zuazo, G.R. Castro, *Nucl. Instrum. Methods Phys. Res. A, **547**, 64-72 (2005)*.

2. J. Rubio-Zuazo, P. Ferrer, G.R. Castro, *J. Electron Spectrosc. Relat. Phenom., **180**, 27-33 (2010)*.

3. M. Gorgoi, F.Schäfers, S.Svensson, N.Mårtensson,” J. Electron Spectrosc. Relat. Phenom.,, **190**, 153-158 (2013)

4. C. Kunz, S. Thiess, B. Cowie, T.-L. Lee, J. Zegenhagen, *Instrum. Methods Phys. Res. A, **547**, 73-86 (2005)*.

5. J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8** 129–137 (1976).

6. M.B. Trzhaskovskaya, and V.G. Yarzhemsky, At. Data and Nucl. Data Tables,**119** (2018) 99–174

3:20pm **AS+BI+CA+LS-TuA-4 Interfacial Photochemistry of Pyruvic Acid in Atmospheric Chemistry***, **Yanjie Shen**, Y Fu,* Pacific Northwest National Laboratory*; X Yao,* Ocean University of China*; Z Zhu,* Pacific Northwest National Laboratory*; X Yu,* Earth and Biological Sciences Directorate

Presentation Summary:

This presentation will show our latest results of pyruvic acid photochemical aging in dry and liquid surface analysis s using time-of-flight secondary ion mass spectrometry.

Abstract

Pyruvic acid is widespread in fogs, aerosols, and clouds. The sunlight driven reaction pathways of pyruvic acid in the air-liquid interface are more elusive compared to its well-known gas and bulk phase chemistry in the atmosphere. We investigated photochemical aging products from pyruvic acid after different UV photolysis times up to 8 hours in dry and liquid samples using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Both ToF-SIMS spectral and spectral principal component analysis (PCA) were used to study the surface photochemical aging products among various photochemical aging samples. A number of aging products were observed in dry samples indicating the importance of interfacial reactions[1]; however, the dry sample analysis cannot fully represent the air-liquid interfacial chemistry of pyruvic acid. Therefore, we used our unique liquid surface molecular imaging approach enabled by the SALVI microfluidic reactor to study the air-liquid interface. The *in situ* liquid SIMS observations show photochemical products of pyruvic acid at the air-liquid interface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with submicrometer spatial resolution. In addition, SIMS three-dimensional chemical mapping provides visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant as illustrated in the chemical spatial mapping with increased photolysis time. Our study of the pyruvic acid aqueous surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosols (SOAs) in atmospheric chemistry.

Key Words: pyruvic acid, photochemical, dry SIMS, liquid SIMS, air-liquid interface, oligomer, water cluster, SOA.

References:

1.Fu, Y.; Zhang, Y.; Zhang, F.; Chen, J.; Zhu, Z.; Yu, X.-Y., Does interfacial photochemistry play a role in the photolysis of pyruvic acid in water? *Atmospheric Environment* **2018,***191*, 36-45.

4:20pm **AS+BI+CA+LS-TuA-7 Nanoscale Tomographic Mapping the Liquid-Solid Interface with Cryo-APT***, **Daniel Perea**, D Schreiber, J Evans, J Ryan,* Pacific Northwest National Laboratory **INVITED**

The liquid-solid interface plays an essential role in many phenomena encountered in biological, chemical, and physical processes relevant to both fundamental and applied science. However, study of the liquid/solid interface at the nanoscale is challenging as liquids are generally incompatible with many analytical techniques that require high to ultrahigh vacuum conditions. One strategy to probe the liquid-solid interface is to cryogenically freeze the liquid into solid form to preserve local ionic chemistry gradients and surface composition within a solid structure, making it more amendable to vacuum-based analyses such as Atom Probe Tomography (APT). However, the regular application of APT to hydrated materials is lacking due to challenges in preparing the necessary nanoscale needle-shaped specimens using a FIB-SEM and the subsequent environmentally-protected transfer of the frozen specimens to the APT instrument for analysis. In this presentation, I will discuss the development of a FIB-based site-specific liftout and attachment scheme of cryogenically cooled specimens involving a combination of redeposition and overcoating of organic and organometallic molecules. A modified commercially-available specimen suitcase shuttle device and an environmental transfer hub vacuum chamber at PNNL is used to facilitate environmentally-protected specimen transfer between the cryo FIB and the APT tool, allowing for the first time, APT analysis of a water/solid interface in 3D to reveal the complex nanoscale water-filled porous network of corroded glass. Application of this unique specimen preparation approach to biological specimens will also be discussed.

5:00pm **AS+BI+CA+LS-TuA-9 Characterization of Electronic Materials using Low Energy Inverse Photoemission Spectroscopy***, **Benjamin Schmidt**, J Newman, J Mann, K Artyushkova, L Swartz,* Physical Electronics*; M Terashima, T Miyayama,* ULVAC-PHI Inc., Japan

The development of complex electronic materials in areas such as batteries, solar cells, and flexible display panels require a detailed knowledge of the electronic band structure in order to achieve desired performance. A few of the material properties of interest are electron affinity, work function, ionization potential, and bandgap. Photoemission spectroscopic techniques such as Ultraviolet Photoelectron Spectroscopy

(UPS) and Inverse Photoemission Spectroscopy (IPES) have traditionally been used to measure these values.

Organic electronic materials are growing in popularity due to lower costs of production and the ability to create interesting mechanical structures. However, they are susceptible to chemical damage with prolonged exposure to high-energy electron beams during analyses, which can affect the measured properties.

Low Energy Inverse Photoemission Spectroscopy (LEIPS) is a variant of IPES but uses an incident electron beam at lower energy than traditional IPES (< 5 eV vs. ~10 eV, respectively), making it less damaging for organic materials. In this talk, the operating principles of LEIPS will be discussed. Several material system examples will be shown, including films of C60 and copper phthalocyanine (CuPc).

5:20pm **AS+BI+CA+LS-TuA-10 Deconvolution of Atom Probe Tomography on Nanomaterials for Renewable Energy***, **Margaret Fitzgerald**, M Dzara, D Diercks,* Colorado School of Mines*; N Leick, S Christensen,* National Renewable Energy Laboratory*; T Gennett, S Pylypenko,* Colorado School of Mines

Technologies for hydrogen-based economy rely heavily on advancements in development of nano-structured materials. Nano-materials used in applications for energy conversion, storage and production have unique, desirable properties because of their intricate chemistries and morphologies, however this makes them difficult to characterize using traditional techniques. Of specific interest is elucidation of the surface properties and identification of differences between surface and bulk composition. This work features Atom Probe Tomography (APT) paired with other techniques that enable multi-scale characterization in 2D and 3D as a promising approach to create a more complete picture of the complexities of nano-structured materials.

APT is an incredibly powerful tool that has been used to render sub-nanometer-resolution, 3D reconstructions of metallic and, more recently, ceramic samples to enhance the understanding of local composition variations, such as around grain-boundaries and precipitates. This presentation outlines the procedures and considerations for expansion of APT towards analysis of nano-structured materials used for catalysis and hydrogen storage. Challenges related to both APT specimen preparation, APT analysis, and data reconstructions will be discussed. Specific considerations that will be addressed include sample pre-screening for mass spectrometry peak overlap, substrate and encapsulation material selection based on field evaporation compatibility, and prevention of sample damage for air- and beam-sensitive materials. In order to produce accurate 3D reconstructions of the APT data for these samples, initial assessment of a two-dimensional morphology of these materials is made using scanning transmission electron microscopy (STEM) and elemental distributions are acquired with energy dispersive x-ray spectroscopy (EDS). Surface chemistry of the sample is determined using X-ray Photoelectron Spectroscopy (XPS) in order to correlate surface chemistry between APT data and quantified XPS chemical ratios. This talk will provide evidence of cross-correlation across multiple techniques and integration of 2D and 3D data to provide a pathway for understanding these complex materials beyond traditional capabilities.

5:40pm **AS+BI+CA+LS-TuA-11 Mass Spectrometric Investigation of Ion Solvation in Liquids, a Comparison of *in situ* Liquid SIMS to Regular ESI-MS***, **Yanyan Zhang**,* Institute of Chemistry, Chinese Academy of Sciences, China*; D Baer, Z Zhu,* Pacific Northwest National Laboratory

Ion solvation plays very important roles in many important biological and environmental processes. Mass spectrometry (MS)-based methods have been used to investigate this topic with molecular insights. To study ion solvation, ionization processes should be as soft as possible in order to retain solvation structures. An *in situ* liquid secondary ion MS (SIMS) approach developed in our group has been recently utilized in investigations of Li ion solvation in nonaqueous solution, and it detected a series of solvated Li ions.[1] As traditionally SIMS has long been recognized as a hard ionization process with strong damage occurring at the sputtering interface, it is very interesting to study further how soft *in situ* liquid SIMS can be. In this work, we used halide ion hydration as a model system to compare the ionization performance of the *in situ* liquid SIMS approach with regular electrospray ionization MS (ESI-MS). Results show that, although ESI has been recognized as a soft ionization method, nearly no solvated halide ions were detected by regular ESI-MS analysis, and only strong signals of salt ion clusters were seen. As a comparison, in liquid SIMS spectra, a series of obvious hydrated halide ion compositions could be observed.[2] Our findings demonstrated that the *in situ* liquid SIMS approach is surprisingly soft, and it is expected to have very broad applications on investigation of various weak interactions and many other interesting chemical processes (e.g., the initial nucleation of nanoparticle formation) in liquid environment.

References:

[1] Zhang, Y.; Baer, D.; Zhu, Z.*, et al., “Investigation of Ion-Solvent Interactions in Non-Aqueous Electrolytes Using *in situ* Liquid SIMS”, *Anal. Chem.*, **2018**, *90*, 3341–3348.

[2] Zhang, Y.; Zhu, Z.*, et al., “*In Situ* Liquid SIMS: A Surprisingly Soft Ionization Process for Investigation of Halide Ion Hydration”, *Anal. Chem.***2019**, *published online,* DOI: 10.1021/acs.analchem.8b05804.

6:00pm **AS+BI+CA+LS-TuA-12 Characterizing the Thickness and Physical Properties of Nearly Ideal Zirconium Oxide Surfaces Using Ellipsometry, ESCA, Profilometry and FIB***, **Edward Gillman**,* Naval Nuclear Laboratory

Zirconium alloys are used in nuclear reactor cores due to their small neutron scattering cross-section and corrosion resistance. Corrosion of zirconium alloys results in the formation of a protective oxide layer that the corrosion species must travel through in order to continue the corrosion process. This oxide prevents further oxidation of the metal, slowing down the reaction rate. Characterizing this important oxide film on a metal is difficult. A number of analytical techniques are used to better understand the properties and growth of this oxide film. To insure that reliable information is reported, the thickness and physical properties of zirconium oxide deposited on a single-crystal silicon wafer by magnetron sputtering has been investigated. Data obtained from Electron Spectroscopy for Chemical Analysis (ESCA), profilometry, ellipsometry and Focused Ion Beam (FIB) experiments are all self-consistent with each other. This validates the utility of these measurements for the characterization of the oxide observed on metallic surfaces.

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