

# Thursday Evening Poster Sessions, November 2, 2017

## Applied Surface Science Division Room Central Hall - Session AS-ThP

### Applied Surface Science Poster Session

#### AS-ThP-1 Depth Profiling Adventures in the Non-Semiconductor Chemical Industry, *Kathryn Lloyd, J Marsh, DuPont*

Until recently, technology development for SIMS depth profiling was centered around flat semiconductor wafers. Sputter rates could be determined using standards and doped standards. Experimental protocols continue to be optimized, but figures of merit are for the most part understood.

With the expansion of computer memory and disk space, sophisticated vendor and third-party software, and new cluster beam sputter sources, SIMS (specifically ToF-SIMS) depth profiling is now being applied to distinctly non-flat, standards-defying, or just structurally-complex systems. In the realm of inorganic depth profiling, the quasi-parallel spectral acquisition compared to quadrupole mass analyzers and the use of multivariate statistics can mitigate many problematic mass interferences. For organic/polymeric systems such as fibers, resins, and coatings, huge Argon gas cluster sputtering enables molecular detection of sub-surface species. Hybrid systems such as OLEDs and paints continue to present challenges because of the different sputtering conditions needed for the different layers. For all of these samples, the ability to visualize the depth profiling data in 3D graphics is very powerful.

One could argue that these experiments are less true "depth profiling" experiments and more "just sputtering" to obtain sub-surface chemical information. In any case, this presentation will show examples of sputtering ToF-SIMS applications in an industrial environment that have been made possible through the implementation of new Argon cluster sputter beams and/or the use of multivariate statistics.

#### AS-ThP-2 High-energy Cluster Ions - Minimising Depth Profiling Artifacts for Solid-state Electrolytes, *J Counsell, Kratos Analytical Limited, UK; Chris Moffitt, Kratos Analytical Ltd; A Pearse, University of Maryland, College Park; C Blomfield, S Coultas, Kratos Analytical Limited, UK; G Rubloff, University of Maryland, College Park*

Classical lithium ion batteries rely on a liquid electrolyte however there have been significant developments towards replacing liquid electrolytes with solid state thin-films. Thin-film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical liquid electrolyte batteries [1]. In order to construct a thin film battery it is necessary to fabricate all the battery components, such as an anode, a solid electrolyte, a cathode and current leads into a multi-layered thin film. Lithium phosphorous oxynitride (LiPON) is widely used as the electrolyte in solid state micro-batteries due to low electronic conductivity, increased durability to cycling and ease of preparation.

Here we will use conventional surface analysis techniques of XPS and sputter depth profiling to understand the surface and bulk chemistry of LiPON thin films formed via atomic-layer deposition (ALD) [2]. XPS yields quantitative information regarding the elemental composition of the near surface region to a depth of <10 nm. The elemental composition as a function of depth is probed and comparisons are made between conventional monatomic depth profiling and cluster depth profiling. We will also analyse complete battery stacks in their virgin and cycled states and discuss changes in elemental distributions at the interfaces between the electrodes and the solid electrolyte.

We demonstrate that the use of monatomic Ar ions is unsuitable for profiling materials with mobile light elements (Li) as the build-up of positive charge causes migration leading to erroneous depth composition. An alternative is proposed whereby the analyst uses 20 kV high-energy cluster ions in an attempt to mitigate the effects of ion migration and thereby improving confidence in the validity of the results.

[1] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, M. Armand, *Nat. Energy* 2016, 1, 16030.

[2] A. Kozen, A. Pearse, G. Rubloff, C-F Lin, M. Noked, *Chem. Mater.*, 2015, 27, 5324–5331

#### AS-ThP-3 The Internal Composition and Structure of Fish Scales Investigated by ESCA and SEM, *Gerry Hammer, S Murcia, E Lavoie, L Gamble, D Arola, D Castner, University of Washington*

Fish scales are one example of a biological structure that provides physical protection without restricting the flexibility or mobility of the bearer. These types of structures are often complex composites and have attracted interest in the field of biomimetics, including the areas of personal armor and protective equipment. Elasmoid fish scales consist of mineral and organic materials, including hydroxyapatite, calcium carbonate and collagen fibers. Scales from pirarucu (*Arapaima gigas*), tarpon (*Megalops atlanticus*), and carp (*Cyprinus carpio*) were fixed, dehydrated, mounted in epoxy and microtomed to expose cross-sections. These sections were analyzed using ESCA and SEM to determine the composite structure and characterize the variations in composition through the scale thickness. ESCA images were obtained for a qualitative evaluation, and spectra from small area analyses provided information for a complementary quantitative analysis. The collagen fibers in the pirarucu were stacked in plies with a rotation angle of 90° between them, while in the tarpon and carp the rotation angle was 75° between successive plies. ESCA images and small area analyses showed the changes in composition between the mineralized limiting layer (LL), the mineral reinforced collagen fibers of the external elasmoidine (EE) layer, and the collagen fibers of the internal elasmoidine (IE) layer.

#### AS-ThP-4 Ambient Pressure X-ray Photoelectron Spectroscopy of the III-V Semiconductor/Water Interface, *Pitambar Sapkota, S Ptasinska, University of Notre Dame*

Along with the intense study of semiconductors for promising photovoltaic application, these materials are also used for harvesting solar energy, where energy is stored in the form of chemical fuels. This is through photoelectrochemical (PEC) solar cells, which are being extensively explored recently. Performance and stability of such PEC devices largely depend on the electronic properties and chemistry at the interface of semiconductors and water. Oxidation of the semiconductor surface during operation has been shown to be the major cause of degradation in action and durability of such devices. This research has studied the interactions of water with the III-V semiconductor surface during operando condition using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The results obtained through this study help to determine the reaction pathway leading to oxidation and its extent on the surface. This knowledge can provide deeper insight into the tuning parameters necessary to obtain better operating and more lasting PEC devices.

#### AS-ThP-5 Spectroscopic and Structural Studies of Iron Gall Ink, *Karen Gaskell, A Ponce, University of Maryland, College Park; L Brostoff, Library of Congress; S Gibbons, B Eichhorn, P Zavalij, University of Maryland, College Park; C Viragh, The Catholic University of America; S Alnemrat, J Hooper, Naval Postgraduate School at Monterey*

Iron gall inks were the major writing medium from the middle ages through the 19th Century in the Middle East and Europe, and are present in hundreds of thousands of important cultural heritage objects worldwide, including books, manuscripts and artistic drawings. Iron gall ink depending on its preparation is well known for its potentially corrosive effect on paper or other writing medium, over time, changes in temperature and humidity can accelerate this degradation resulting in the worst case, complete loss of documents. The major ingredients of iron gall ink are iron salts, most often iron sulfate, tannic acids derived from vegetable sources such as gall nuts and gum arabic used as a binder. Despite much research in this area the chemistry of iron gall ink is still poorly understood. Through spectroscopic and structural measurements of synthesized model compounds and authentic documents combined with aging studies, we conclusively show that the main colorant of iron gall ink is an amorphous form of Fe(III) gallate-xH<sub>2</sub>O (x = ~ 1.5–3.2). Comparisons between experimental samples and historical documents by XPS, Raman and IR spectroscopy, XRD, and Mössbauer spectroscopy confirm the relationship between the model and authentic samples.

#### AS-ThP-7 Multicomponent Patterned Ultrathin Carbon Nanomembranes by Laser Ablation, *Daniel Rhinow, Max Planck Institute of Biophysics, Germany; N Frese, Bielefeld University, Germany; J Scherr, Goethe University Frankfurt, Germany; A Beyer, Bielefeld University, Germany; A Terfort, Goethe University Frankfurt, Germany; A Götzhäuser, Bielefeld University, Germany; N Hampp, Philipps Universität Marburg, Germany*

Carbon nanomembranes (CNMs) are two-dimensional materials obtained by electron beam-induced crosslinking of self-assembled aromatic precursors. Irradiation of aromatic SAMs with low-energy electrons leads

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to the formation of graphene-like molecular sheets with a thickness of only 1 nm. CNMs made from a single precursor molecule are in principle uniform. We have developed a method for the fabrication of internally patterned CNMs with locally varying chemical and physical properties. Photothermal patterning of SAMs enables the fabrication of arbitrary structured monolayers with lateral dimensions up to centimeters. We have used direct laser patterning to produce patterned aromatic SAMs, which were subsequently converted to CNMs by electron irradiation. Patterned CNMs have been analyzed by helium ion microscopy (HIM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Our experiments confirm that the structure of patterned CNM is preserved upon electron-induced crosslinking and transfer to different substrates.

## AS-ThP-8 Characterization of Laser-Treated Al-Alloy Surfaces, *Harry Meyer, D Leonard, A Sabau*, Oak Ridge National Laboratory

Lightweight materials, such as aluminum alloys, find increasing use in both automotive and aerospace applications. A key requirement for their use is effective surface cleaning and texturing techniques to improve the quality of the structural components. Work at ORNL focuses on the a novel surface treatment method using laser interferometry produced by two beams of a pulsed Nd:YAG laser. Operating at 10Hz of frequency, this technique has been used to clean aluminum surfaces, and at the same time creating periodic and rough surface structures. The influences of beam size, laser fluence, wavelength, and pulse number per spot are currently under investigation. Metallic aluminum is very reactive with atmospheric oxygen and quickly forms a native oxide surface layer. This layer of oxide on the surface can affect further manufacturing processes, such as welding, and must be removed prior to any joining step. Without proper surface preparation, seams and joints are susceptible to increased wear, degradation and, in some cases, catastrophic failure. There are many methods for removing aluminum surface oxides, including mechanical (i.e. abrasive wear) and chemical stripping, generally used for complex part geometries. Despite its effectiveness, chemical stripping also introduces higher costs associated with environmental protection and hazardous-waste management. Aluminum and aluminum alloy surfaces can be cleaned using high-energy laser pulses (nanoseconds to milliseconds range) and is accomplished mainly by surface melting and ablation. This method is a non-contact process without abrasion and chemical impact and the controllability offered by using lasers enables high-precision removal of surface oxides and other contaminants in the range from sub-micrometers to several millimeters. The process being optimized at ORNL is using a 2-beam method that not only cleans the surface for joining but textures the surface in a periodic manner. This poster present preliminary surface characterization results for the cleaning of Al-alloy surfaces. Results from optical and electron microscopies, scanning Auger microanalysis, x-ray photoelectron spectroscopy, and contact angle measurements on as received and laser-treated Al-2024 alloy surfaces will be shown. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

## AS-ThP-11 Space Weathering Effects on Ceres: Novel Application of Surface Analytical Techniques to Questions in Planetary Science, *Gerard Rodriguez Lopez, C Dukes, C Bu*, University of Virginia; *L McFadden*, NASA Goddard; *J Li*, Planetary Science Institute; *O Ruesch*, NASA Goddard

**Introduction:** The solar wind plasma continuously streams from the Sun, interacting with the surfaces of airless bodies throughout the solar system. Sulfates, suggested by the thermal emission [1], and carbonates, identified by the 3.4 and 4.0  $\mu\text{m}$  absorption features [2] on the surface of Ceres by NASA's Dawn spacecraft, will be exposed to solar wind  $\text{H}^+$  and  $\text{He}^+$  at  $\sim 1$  keV/amu irradiation. We investigate the stability of these salts under 4 keV  $\text{He}^+$  irradiation as solar-wind proxy at the low pressure/temperature conditions found in the Main Asteroid Belt.

**Experiment:** Anhydrous  $\text{MgSO}_4$  and  $\text{Na}_2\text{CO}_3$  powders are pressed into pellets and compositions are confirmed by X-ray diffraction. We measure diffuse optical reflectance prior and subsequent to irradiation through 0.2-2.5  $\mu\text{m}$  ( $\lambda = 1050$ ) and 0.6-16  $\mu\text{m}$  (Thermo Nicolet 670). Pellet samples are then introduced to ultra-high vacuum ( $10^{-9}$  Torr) and maintained at 110 K and effects of *in situ* 4 keV  $\text{He}^+$  irradiation are monitored by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy. Variations in surface composition and chemistry are identified and quantified as a function of fluence.

**Results:** Solar wind type ion irradiation of  $\text{MgSO}_4$  damages the crystal structure, preferentially removing oxygen along with sulfur. XPS measurements imply the formation of  $\text{MgO}$  after  $5 \times 10^{17}$   $\text{He}^+$   $\text{cm}^{-2}$  ( $\sim 15,000$  years at 2.7 AU); a small shoulder on the sulfur peak suggests the presence

of trapped  $\text{SO}_2$ , also confirmed by the IR feature observed at  $\sim 7.8 \mu\text{m}$  with irradiation. McCord et al. (2001) provides a potential decomposition pathway for  $\text{MgSO}_4$  to  $\text{SO}_2$  consistent with our observations. We observe secondary ion ejection ( $\text{Mg}^+$ ,  $\text{MgO}^+$ ,  $\text{O}^+$ ,  $\text{OH}^+$ ,  $\text{H}^+$ ,  $\text{S}^+$ , and  $\text{SO}^+$ ) from  $\text{MgSO}_4$  with He-impact, and neutral spectra show loss of  $\text{SO}_2$ . Spectral darkening and reddening in the UV-Vis region is observed by *ex situ* optical spectroscopy after irradiation.

Bright  $\text{Na}_2\text{CO}_3$  deposits darken as a function of solar wind exposure in the visible spectrum on a timescale of 1-10 thousand years. Visible darkening, caused by enhancement in surface Na as C and O are preferentially removed, can be completely reversed by exposure to  $\text{H}_2\text{O}$  vapor. For Ceres' bright regions, this suggests that brightest areas are likely to be the most recent material deposits or the most recently exposed to water.

**Acknowledgements:** We thank the NASA SSW and NSF-Astronomy programs. I thank Dr. Petra Reinke for her support and encouragement.

**References:** [1] Bu et al (2017) GRL (submitted) [2] Palumbo et al (2016)

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#2328 [5] Lane (2007) Am. Mineral 92, 1-18 [6] McCord et al (2001) JGR 106, 3311-

3319.

## AS-ThP-13 Combustion Soot-derived Carbon Nanostructures: Microscopic and Spectroscopic Investigations, *Ich Tran, T Aoki*, University of California, Irvine; *J Beardslee, C Moffitt*, Kratos Analytical, Inc.

The formation and fundamental properties of carbon nanostructures from combustion soot are investigated. Chemical and ultrasonic treatments were employed to extract elemental carbon nanostructures from raw soot obtained from combustions of biomass waste materials, as well as from ethylene flames. A combination of transmission electron microscopy and photoelectron spectroscopy/imaging techniques, was used to elucidate the relationships between the formation of combustion soot derived carbon nanostructures and their structural, chemical and electronic properties. These experimental data are correlated to models and mechanisms of soot formation and growth in combustion processes.

## AS-ThP-14 Probing the Chemical-State of Zinc centers in unknown Environments: A Comparison of Conventional and Core-core-core Auger Parameter Analyses, *William Kaden*, University of Central Florida

Citrus greening is a major problem for the agricultural community in the United States. Afflicted trees typically die within a few years of infection and produce fruit that is green, misshapen, and bitter to the taste. To mitigate the deleterious effects of this epidemic, a Florida-based team of researchers have developed a spray-dispersible bactericide known as Zinkicide™, which consists of zinc-containing nanoparticles capable of entering and freely traversing the phloem-containing vascular system of infected trees to selectively kill bacteria within infected cells. While controlling the size of the particles is of key importance to their membrane transverability, the chemical-state of the zinc centers is believed to be of key importance to controlling the resultant chemical interactions with the bacteria.

Having demonstrated proof-of-concept utility with laboratory-scale quantities of bactericides created from reagent-grade precursors, TradeMark Nitrogen has since begun scale-up efforts using agricultural-grade precursors. Given the importance of chemical-state on the bacteriicidal properties of the nanoparticulates, detailed characterization of the powders is of great importance. Unfortunately, traditional core-level XPS analysis of zinc centers is not sufficient for such characterization due to the relative insensitivity of the most intense transition (Zn 2p), which results in shifts too small to distinguish Zn in chemical compositions as disparate as  $\text{Zn}^0$  and  $\text{ZnO}$  for example.

Due to this core-level insensitivity, most reported photoemission analysis of Zn makes use of an associated Auger transition to allow for Wagner plot comparisons to libraries of Zn in known compositions. Such analysis allows for peak assignments through both qualitative and quantitative comparisons with reference data, but is limited in its ability to disambiguate the chemical-states of Zn in environments not perfectly reproducing those of previously measured control samples due to the non-extrapolatable nature of Auger parameter measurements incorporating core-valence-valence transitions. By contrast, appropriately chosen combinations of core-level XPS and core-core-core Auger lines have been shown to provide more reliable estimates of final-state contributions to XPS peak shifts, thereby allowing for direct initial-state interpretation of

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those shifts (i.e. direct correlation between the extent of the final-state corrected XPS shifts and the degree of oxidation). In this talk, we will present XPS and Auger data sufficient to compare results from both types of analyses on both reference and various Zinkicide™ samples made available for analysis by TradeMark Nitrogen.

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