Applied Surface Science
Room: C2 - Session AS-FrM

Practical Surface Analysis
Moderator: S.R. Bryan, Physical Electronics

8:20am **AS-FrM1 Combined XPS and AES Characterization of Nano Structures Developed for Advanced Energy Conversion and Storage Materials**, ***C. Hitzman***, Stanford University **INVITED**

Ultra-Thin films, Nano-Particles and Nano-Wires are at the center of research for new materials for use in Photonics, Nano-Electronics and Advanced Energy Conversion and Storage. Metals, Semiconductors, Glasses and Polymers are all being investigated for these applications. Understanding the structure, composition and chemistry of these new materials is essential in advancing their development.

X-ray Photoelectron Spectroscopy (XPS) is one of the most commonly used surface techniques for quantitative measurements of elemental composition and specific chemical information of surface constituents. Angle Resolved XPS and XPS combined with ion sputtering can provide information beyond the surface of the material. There are some limitations, however, in the special resolution of XPS.

Auger Electron Spectroscopy (AES) can provided elemental information with high spatial resolution. This is extremely useful in obtaining localized information from Nano Particles and Nano Wires.

The combination of the XPS and AES techniques can further advance the development of these new material. In this presentation we will look at complimenting and correlating data obtained by XPS and AES from a variety of advanced materials from a host of application areas.

9:00am **AS-FrM3 Investigation of Internal Structure of Drug Products by TOF-SIMS and CT**, ***X. Dong***, *C.A.J. Kemp*, Eli Lilly and Company

The properties of API and excipients can influence the manufacturing process and the quality attributes of the dosage form. It is known that particle size, shape, and agglomeration of the drug substance and excipients affect flow properties, dissolution behavior, dose uniformity and bioavailability of the formulation. Therefore, there is a key interest in pharmaceutical development to understand how the ingredients of the formulation are blended in the various stages of the production process, as well as how various components distribute in solid dosage form. TOF-SIMS has been applied to provide chemical images for various drug products. Due to the surface sensitivity of this technique, the images could be affected by potential smearing during sample preparation. To better understand the effect of sample preparation, TOF-SIMS images obtained from drug products are compared with micro-CT images, which are obtained non-destructively. In addition, the effects of C_{60} sputtering on drug molecule and excipeints, as well as on TOF-SIMS images are also investigated.

9:20am **AS-FrM4 Effectiveness of Passivation Techniques on Hydrogen Desorption in a Pure Tritium Environment**, ***S. Woodall***, *E. Pines, D. Valles-Rosales*, New Mexico State University

This research compared protium outgrowth of different passivation surfaces in a low pressure environment. Tritium is a radioactive isotope of hydrogen. It is used as a fuel in fusion reactors, a booster material in nuclear weapons and as a light source in commercial applications. When used in fusion reactors, and especially when used in the manufacture of nuclear weapons, purity is critical. For Department of Energy use, tritium is routinely recycled by Savannah River Site and is produced and stored at 99.99% purity. For use elsewhere in the country, it must be shipped and stored, while maintaining the highest purity possible. As an isotope of hydrogen it exchanges easily with the most common isotope of hydrogen, protium. Stainless steel bottles are used to transport and store tritium. Protium, present in air, becomes associated in and on the surface of stainless steel during and after the manufacture of the steel. Therefore, the stainless steel bottles contribute to the contamination of the tritium with protium. This research is to determine how effective different passivation techniques are in minimizing the contamination of tritium with protium. Additionally, this research will attempt to determine a relationship between surface chemistry of passivated steels and protium contamination of tritium.

9:40am **AS-FrM5 Comparison of Supported Catalyst Particle Size Determination by Low Energy Ion Scattering (LEIS) and Transmission Electron Microscopy (TEM)**, *R.A.P. Smith, D. Ozkaya,* Johnson Matthey Technology Centre, UK, *H. Brongersma,* ***T. Grehl***, ION-TOF GmbH, Germany, *H.R.J. ter Veen*, Tascon GmbH, Germany

Particle size determination for supported metal catalysts is vital for the technological improvement of such systems in most areas of catalysis; automotive emission control catalysts, fuel cell materials to name but two. Improved measurements of the dispersion of a supported metal can be fed into product research and development with benefits including improved control of metal deposition and thereby, ultimately, efficient material use, particularly when the supported metal is from the platinum group of metals and so very expensive. The particle sizes of interest for many supported metal catalysts are in a single-digit nanometre range and for many techniques this poses a problem.

TEM is one of a limited number of techniques that can be applied in this particle size range but there is an inherent statistical difficulty - the areas studied are limited so might not be truly representative of a well-dispersed material although any information obtained is usually very accurate.

As a laboratory technique rather than large-scale facility such as is often required for effective spectroscopic determination of particle size, LEIS is of great potential use in this area. LEIS signals are directly related to the surface area of a given element that is exposed for the study and a reduction in particle size leads to higher surface area to volume ratio and therefore inherently larger signal from scattered ions for the amount of material present. In addition, although the single outermost layer of a surface is the principal signal of interest, a signal due to ions scattered from deeper layers can be measured and is useful for determination of extremely thin (up to 10 nm) layers. This makes the technique useful for electronics applications but it can also be applied to characterise how "thick" a particle is, leading to a second method of particle size determination. For these two reasons, smaller particles yield good information when studied by LEIS. The technique is a large-area (1 mm scale) technique so provides statistically representative average information. LEIS also has advantages over TEM in that it works just as easily on supports with heavy elements (zirconia, ceria) as light elements (carbon, alumina).

In this presentation we show results of a comparative study of LEIS and TEM used for the characterisation of model fuel cell materials, specifically platinum supported on carbon with a range of particle sizes under 10 nanometres. The results show that LEIS is an effective laboratory technique that can provide excellent characterisation data on small particles that can be correlated with other techniques to improve understanding of commercial systems.

10:00am **AS-FrM6 Characterization of Organic Light Emitting Devices Via Surface Analysis and Electron Microscopy**, ***D.J. Gaspar***, *A.S. Lea, A.B. Padmaperuma, Z. Zhu, D.W. Matson, L. Wang,* Pacific Northwest National Laboratory, *J. Berry, D.S. Ginley*, National Renewable Energy Laboratory

The development of energy efficient organic light emitting devices (OLEDs) for solid state white lighting is a goal of the US Department of Energy. Key challenges facing the development of these materials include materials stability and device lifetime, particularly for blue phosphorescent devices, a necessary component of a white OLED device. Due to the high exciton energy necessary to generate blue light (i.e., quenching and side reactions more easily occur), the stability and lifetime of these devices is a particular challenge. There are many mechanisms by which a device may fail, including interfacial and bulk reactions, diffusion of components within or between layers, and structural and/or phase changes within one or more components. A great deal of work has been done to elucidate mechanisms of degradation, including through chemical and physical failure analysis of components and devices. We present here some of our work to elucidate chemical and physical changes in OLEDs devices and components using surface analysis and electron microscopy. We have used various tools including X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS), focused ion beam (FIB) combined with both electron microscopy (scanning and transmission), X-ray diffraction and atomic force microscopy (AFM, including conductive AFM). This talk will focus on characterization of devices incorporating new materials including transparent conducting oxides, host, and electron- and hole-transporting materials.

10:20am **AS-FrM7 Structure and Composition of Plasma Treated Polystyrene Surfaces Determined by Complementary Analytical Techniques**, ***P. Mack***, *R.G. White, T. Carney,* Thermo Fisher Scientific, UK, *E.H. Lock, S.G. Walton,* Naval Research Laboratory, *D.Y. Petrovykh*, Naval Research Laboratory and University of Maryland

Plasma-treatment of polymers produces materials that exhibit a wide range of surface compositions, properties, and structures. A new low-energy plasma treatment method aims to modify only the top few nanometres of polymer films, producing surfaces that pose challenges and offer opportunities for quantitative surface analysis. Using a variety of complementary analytical techniques maximizes the information available to the analyst.

High-quality polystyrene films were spin-coated onto silicon substrates and treated with low-energy plasmas generated by electron beams in different environments, including oxygen, nitrogen, and SF6. Atomic Force Microscopy was used to determine surface roughness and contact angle measurements were used to determine the hydrophobicity of the plasma-modified surfaces. The Thermo Scientific Theta Probe, an XPS system that provides a unique parallel-detection capability for angle-resolved XPS (PARXPS) and REELS measurements, was used to investigate the chemical and structural transformations produced by different plasmas.

The chemical changes produced by plasma treatments were examined by high energy resolution XPS, and PARXPS data were analyzed using maximum-entropy calculations to obtain non-destructive depth profiles of these chemical changes. Complementary REELS measurements were used to examine the level of carbon unsaturation at the uppermost surface of each of the plasma modified polystyrene films. The non-destructive PARXPS depth profiles were also compared with high-resolution low-energy ion sputter profiles measured in a Thermo Scientific K-Alpha system. The depth profiles obtained using several surface analysis methods confirmed that the chemical changes produced by the low-energy plasma modification are confined to the top 2–3 nm of the polymer surfaces. The observed depth distribution of unsaturated carbon species is also consistent with polystyrene surfaces undergoing "hydrophobic recovery" after treatments in oxygen and nitrogen plasmas.

This work was supported by the Office of Naval Research.

E. H. Lock is NRL/NRC Postdoctoral Research Associate.

10:40am **AS-FrM8 An Investigation of Detection Limits and Common Interference Factors in Depth Profiling Hydrogen and Deuterium by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Z. Zhu***, *V. Shutthanandan*, Pacific Northwest National Laboratory

Hydrogen depth distribution is very important information in today's novel material research. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for this task for quite a while. Normally, dual beam strategy, in which a cesium ion beam is used for sputtering, and a primary ion beam (Ga^+, In^+, Au^+, Bi^+ …) is used for measurement, is applied in hydrogen depth profiling. Residual gas in vacuum chamber has been found to significantly interference SIMS hydrogen depth profiling, so that deuterium is introduced to substitute hydrogen for SIMS analysis if feasible. Apparently, the information of detection limits and common interference factors are very important for ToF-SIMS users, but such information was not easily available. In this work, we investigated detection limits of hydrogen and deuterium in four widely used materials, including silicon wafer, quartz, zinc oxide and titanium oxide. Deuterium ions were quantitatively implanted into these samples, and they were used as the standard to evaluate detection limits of both hydrogen and deuterium. It is found that hydrogen detection limit is about 100-400ppm, limited by residue gas interference. On the other hand, detection limit of deuterium can be as low as 1-10ppm due to no interference. These results will be discussed along with some common interference factors.

11:00am **AS-FrM9 Ultra-Low-Angle-Microtomy to Prepare Fuel Cell Membrane Electrode Assemblies for XPS Analysis**, *K.S. Reeves, K.L. More,* Oak Ridge National Laboratory, *R.G. White, T.S. Nunney, A.E. Wright,* Thermo Fisher Scientific, UK, ***H.M. Meyer III***, Oak Ridge National Laboratory

Membrane electrode assemblies (MEA) were examined before and after use in a hydrogen fuel cell. MEAs consisted of anode and cathode (both comprised of carbon and Pt-catalyst) separated by a polymeric proton exchange membrane (PEM) made from Nafion®. Of particular interest is through-depth compositional uniformity of the membranes after use. PEMs are typically 20-50 microns thick and as such, the use of surface sensitive techniques to probe their through-depth composition requires unique sample preparation. Traditional Ar-ion depth profiling is not possible since even low energy (200-500 eV) Ar ions disrupt the polymer structure and chemical bonding. Polyatomic sputter systems developed for etching polymer surfaces without imparting damage are also of little use due to low sputter rates (~0.1 nm/s). Even with a carefully prepared cross-section of the MEA (routinely done for TEM sample prep), only limited information is obtained using the relatively large x-ray spots (10's-to-100's of microns) of most XPS instruments. To probe the inner region of the membrane film, we have developed an ultra-low-angle microtomy (ULAM) sample preparation technique. The ULAM technique is similar to metallographic low-angle lapping and is based on similar methods described by Watts and co-workers [1]. The ULAM-derived taper through a ~25 micron thick membrane effectively extends the cross-section to greater than 400 microns. With this exaggerated cross-section, the 30 micron X-ray spot of our Thermo Fisher Scientific K-Alpha XPS instrument was able to evaluate composition as a function of depth from the anode, across the membrane to the cathode. Core level and VB spectra from the anode, cathode, and membrane components will be presented for a fresh MEA and for the same MEA after 500 hrs of use. To demonstrate the effectiveness of the ULAM technique, data from samples prepared using ULAM will be compared to surfaces of free-standing membrane films and from standard cross-sections.

Research supported by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cell, and Infrastructure Technologies Program. Research at the ORNL SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Dept. of Energy.

[1] S.J. Hinder, C. Lowe, J.T. Maxted, J.F.Watts, Journal of Materials Science **40** (2005) 285-293.

11:20am **AS-FrM10 Acquisition of Quantitative Implant Coverage Maps of Semiconductor Devices with ToF-SIMS**, ***J.A. Ohlhausen***, *M.L. Anderson, J.J. Sniegowski*, Sandia National Laboratories

Secondary Ion Mass Spectrometry (SIMS) is commonly used to acquire quantitative implant profiles in Si-based semiconductors. While dynamic SIMS is the preferred technique due to its sensitivity, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can also be used. The benefit of ToF-SIMS is that the full spectrum is acquired instead of a few selected species. Thus, unexpected species can be retrospectively included in the analysis in post-processing. Typically when measuring implant profiles, SIMS is used to verify a dose and depth distribution as quality control on single wafers from a single fab implant tool. Data from large areas are required to ensure that signal-to-noise levels are reasonable. Occasionally, it is important to measure implant doses on completed or near-completed devices. When this is the case, one no longer has large uniform areas from which to acquire high signal-to-noise data. Instead, the actual implant information is spatially patterned and may be vertically distinct, therefore containing multiple vertical layers. 3D measurements can be performed to determine the spatial distribution of major device constituents, such as metallization lines and insulating paths, but it is very difficult to determine quantitative implant information while measuring the full 3D distribution. This difficulty arises from the inherently low signal-to-noise measurement that cannot be helped by the use of spatial binning. To some extent, these issues can be overcome in ToF-SIMS as the user has independent control over sputter rate and acquisition times. Methods for preparing samples and acquiring data have been developed along with processing protocols to quantify the implant coverage and 3D distribution of implants in semiconductor devices using ToF-SIMS. These procedures, examples and limitations of the technique will be discussed.

†Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:40am **AS-FrM11 Investigations of Interactions Between Hafnium and Carbon During High Temperature Anneals**, ***B.R. Rogers***, *R.D. Geil, B.W. Schmidt*, Vanderbilt University

Results from studies investigating inter-diffusion and reactions occurring between sputtered hafnium layers and carbon substrates will be presented. Hafnium carbide is a ultra-high temperature material of interest to the aerospace and other communities. Our investigations provide fundamental properties such as diffusivities and reaction activation energies needed for materials design. Samples are annealed in inert and vacuum environments and then are characterized using XPS, ion-beam backscattering, AES, and XRD to pull out the parameters of interest.

Authors Index

Bold page numbers indicate the presenter

— A —

Anderson, M.L.: AS-FrM10, 2

— B —

Berry, J.: AS-FrM6, 1
Brongersma, H.: AS-FrM5, 1

— C —

Carney, T.: AS-FrM7, 2

— D —

Dong, X.: AS-FrM3, **1**

— G —

Gaspar, D.J.: AS-FrM6, **1**
Geil, R.D.: AS-FrM11, 2
Ginley, D.S.: AS-FrM6, 1
Grehl, T.: AS-FrM5, **1**

— H —

Hitzman, C.: AS-FrM1, **1**

— K —

Kemp, C.A.J.: AS-FrM3, 1

— L —

Lea, A.S.: AS-FrM6, 1
Lock, E.H.: AS-FrM7, 2

— M —

Mack, P.: AS-FrM7, **2**
Matson, D.W.: AS-FrM6, 1
Meyer III, H.M.: AS-FrM9, **2**
More, K.L.: AS-FrM9, 2

— N —

Nunney, T.S.: AS-FrM9, 2

— O —

Ohlhausen, J.A.: AS-FrM10, **2**
Ozkaya, D.: AS-FrM5, 1

— P —

Padmaperuma, A.B.: AS-FrM6, 1
Petrovykh, D.Y.: AS-FrM7, 2
Pines, E.: AS-FrM4, 1

— R —

Reeves, K.S.: AS-FrM9, 2
Rogers, B.R.: AS-FrM11, **2**

— S —

Schmidt, B.W.: AS-FrM11, 2
Shutthanandan, V.: AS-FrM8, 2
Smith, R.A.P.: AS-FrM5, 1
Sniegowski, J.J.: AS-FrM10, 2

— T —

ter Veen, H.R.J.: AS-FrM5, 1

— V —

Valles-Rosales, D.: AS-FrM4, 1

— W —

Walton, S.G.: AS-FrM7, 2
Wang, L.: AS-FrM6, 1
White, R.G.: AS-FrM7, 2; AS-FrM9, 2
Woodall, S.: AS-FrM4, **1**
Wright, A.E.: AS-FrM9, 2

— Z —

Zhu, Z.: AS-FrM6, 1; AS-FrM8, **2**