Tuesday Evening Poster Sessions, November 8, 2016

Applied Surface Science
Room Hall D - Session AS-TuP
Applied Surface Science Division Poster Session

AS-TuP2 Observing the Effects of Jetting from Sputtering with Both Monatomic Argon and Argon Gas Clusters of Multi-layered Samples Using XPS with Rapid Mapping, ***Timothy Nunney***, Thermo Fisher Scientific, UK; *R. Simpson,* University of Surrey, UK; *C. Deeks, P. Mack, J.P.W. Treacy,* Thermo Fisher Scientific, UK

Nano-scale multi-layered materials are becoming more common, especially in the microelectronics industry. Components used in applications such as flexible electrical circuitry are often made of stacked layers of material. These can include both organic and inorganic materials in a single component. Complications arise in depth profiling these kinds of components when transitioning across the interface between the two material types.

Depth profiling from an inorganic layer to an organic layer can produce an effect known as “jetting”. This is where material from the lower organic layer is rapidly ejected and redeposited around the etch crater, as a result of the high energy penetration of the inorganic material layer. As soon as the organic layer is exposed to the ion beam, the relative high energy ion beam needed to etch the inorganic layer, will cause material from the organic layer to burst out in this jetting effect.

This presentation will demonstrate the effects of jetting on a range of samples, illustrating how the ejection on deposition occurs depending on the type of sample and the ion beam mode type used. It will show differences between monatomic sputtering and cluster sputtering and showcase the benefits of both of these methods of depth profiling. A new form of rapid XPS mapping will be demonstrated allowing the jetting effect to be quickly observed.

AS-TuP3 Multitechnique Surface Analysis for Advanced Microelectronics Materials, ***James Lallo***, Thermo Fisher Scientific; *C. Deeks, P. Mack, T.S. Nunney, J.P.W. Treacy,* Thermo Fisher Scientific, UK

Multitechnique analysis is becoming increasingly common for characterisation of materials. Performing X-ray Photoelectron Spectroscopy (XPS) is now routine in many laboratories to give surface information (0-10 nm). Energy Dispersive X-ray Spectroscopy (EDS or EDX) is also widely used in laboratories to help detect elemental information from smaller areas within the bulk (1-2 µm) of the material. A combination of both EDS and XPS can help to give a wider picture of samples being analysed, giving both elemental and chemical information from both the ‘surface’ and the ‘bulk’ of samples over a wide ranging spatial area.

EDS is often used in microelectronics laboratories to observe if any contaminants are present on the surface. A big contaminant is copper as it has poor adhesion to most insulators, so the ability to observe this is key. We will demonstrate on advanced microelectronic samples that EDS alone is not enough for detecting contaminants such as this, and we will show that XPS is also needed to give the full elemental and chemical details of these types of samples.

This presentation will look at a range of microelectronics samples, and demonstrate by using both XPS and EDS combined on a single system, that no one technique is enough to obtain the full picture of what is in the sample, and show that by having the ability to have both these techniques on a single system, it can provide a wealth of complementary information from the surface and near-surface regions of a material.

AS-TuP4 Surface Analysis of Human Hair – a Multi-technique Approach, ***Sarah Coultas***, *J.D.P. Counsell, C.J. Blomfield,* Kratos Analytical Limited, UK; *M. Openshaw,* Shimadzu - MALDI Technologies Group; *C. Moffitt,* Kratos Analytical Inc.

In 2016, the global hair care market is estimated to be worth about USD 83.1 billion [1] and the size of the market is growing year on year. There are thousands of products available used for both cosmetic and medical purposes and the industry is constantly developing new formulations to improve performance and safety.

There are numerous treatments and modifications made to hair which involve complex surface chemistry. Products contain many ingredients designed to clean, condition, add volume, shine or treat medical conditions such as dandruff to name but a few. Techniques such as XPS, ToF-SIMS and MALDI-ToF have all been used to characterise the surfaces of natural fibres and investigate the efficacy of such treatments. Recent developments in organic depth profiling using argon cluster sources have also been applied to hair samples opening up an interesting extra dimension [2].

Each of the techniques has its own strengths: XPS provides quantitative elemental identification whereas ToF-SIMS and MALDI are rich in molecular information. Here we use the combination of all three to fully characterise the surface treatment of human hair, in particular the application of conditioner. A range of treatment conditions have been studied, including various concentrations of active ingredients and application methods. As well as investigating the distribution with depth using ARXPS and cluster depth profiling we explore the spatial distribution of species via imaging.

[1] http://www.statista.com/statistics/254608/global-hair-care-market-size/

[2] Ishikawa, Kazutaka and Okamoto, Masayuki and Aoyagi, Satoka, Biointerphases, 11, 02A315 (2016)

AS-TuP5 Exploring the Surface and Sub-Surface Nature of Nuclear Graphite, *J.D.P. Counsell, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Limited, UK; ***Chris Moffitt***, Kratos Analytical Limited; *A. Theodosiou,* University of Manchester

Graphite is a key material used in the current generation of UK nuclear reactors. Graphite has been recognised as an excellent neutron moderator and reflector in reactors, allowing sustainable, controlled fission. Contaminants in moderator rods are a major problem as they can act as neutron absorbers. This causes decreased fission and production of unwanted isotopes – a common cause of radioactive waste. The goal of this study is to understand the surface chemistry of graphites used in the UK nuclear industry today.

The surface compositions of Pile grade A (PGA) and Gliso coke graphites are determined using X-ray photoelectron spectroscopy (XPS). The results are compared to commercially available highly-ordered pyrolytic graphite (HOPG). The degree of sp2/sp3 character is determined for each graphite using Auger parameter analysis. Significant variation in sp2 character was observed between graphites. Depth profiling of the surface was performed utilising both monatomic Ar+ ions and cluster Arn+ ions. The mechanics of cluster/monatomic ion bombardment are discussed with respect to surface damage and a suitable method for graphite bulk analysis is proposed.

AS-TuP6 Comparison of Angle Resolved XPS and Ultra-shallow Ar Gas Cluster Depth Profiling of Organometallic Multilayer Materials, ***Simon Hutton***, Kratos Analytical Limited, UK; *T. Bendikov,* Weizmann Institute of Science, Israel; *K. Macak, W. Boxford, S.C. Page, S.J. Coultas, C.J. Blomfield, J.D.P. Counsell,* Kratos Analytical Limited, UK

Angle resolved X-ray photoelectron spectroscopy (ARXPS) is a widely used technique for investigating the depth distribution of species over the first few nanometres of the sample surface. An important property of the technique is that it is non-destructive; the sample is not damaged during the measurement process. This is in contrast to sputter depth profiling where an ion beam removes the surface layer to reveal the underlying material. A major shortcoming of the ARXPS technique is that it provides information only from the surface region of the material. It is limited to the maximum escape depth of the photoelectrons generated during measurement. This limitation is not shared by sputter depth profiling, which can delve deep into the material by employing multiple sputter / analysis cycles.

Chemical damage of the analysed material is an ever present consideration during sputter profiling. One method of reducing this chemical damage is to vary the nature of the sputtering ion. This has proved very successful for organic materials and thin films where massive gas cluster ions have found widespread use. We have previously demonstrated the successful use of massive Ar clusters to sputter depth profile through multi-layer organometallic thin films [1]. In this study we compare the results of non-destructive ARXPS measurements with ultra-shallow sputter depth profiling using massive Ar cluster ions on similar multi-layer organometallic thin films.

The films consist of two well defined and iso-structural osmium and ruthenium polypridyl complexes. These complexes are deposited from solution in a sequence-dependent assembly regime leading to self-propagating molecular assemblies with distinct internal interfaces and composition. [2] The films were assembled on indium tin oxide (ITO) coated glass slides. ARXPS data was collected by tilting the sample with respect to the analyser / X-ray source. The results were processed using a maximum entropy method software package developed specifically for this type of application [3].

Shallow sputter profiles through the thin films were achieved using massive Ar cluster ions with approximately 2000 Ar atoms per cluster. Ion acceleration voltages were kept low to ensure a very low energy per Ar atom and hence limit the sputtered region to the sample surface.

[1] S. Hutton, T. Bendikov, W. Boxford, S. Page, J. Counsell, A. Roberts, C. Blomfield, S. Coultas, *AS-THP3* AVS 62nd International Symposium & Exhibition.

[2] G. de Ruiter, M. Lahav, G. Evmenenko, P. Dutta, D. A. Cristaldi, A. Gulino and M. E. van der Boom, *J. Am. Chem. Soc.* 2013, 135, 16533-16544.

[3] K. Macak*, Surf. Interface. Anal.* 2011.

AS-TuP7 Pd deposited on Al_2O_3 analyzed by Low Energy Ion Scattering (LEIS)*, P. Bruener, T. Grehl,* ION-TOF GmbH, Germany*; **Nathan Havercroft**,* ION-TOF USA*; J.Z. Mundy, G.N. Parsons,* North Carolina State University

Low Energy Ion Scattering (LEIS) is uniquely able to provide quantitative elemental characterization of the outermost atomic layer of a sample. In addition, the LEIS spectra contain information about the composition of the first few nm of the samples. These properties make it an ideal tool for the characterization of thin films, from the initial nucleation stage to complete films. The analysis gives insight into growth modes (island vs. layer-by-layer), growth rates and impurities, as well as accurate information about layer closure.

For the LEIS analysis, noble gas ions with kinetic energy of a few keV are scattered by individual atoms in the sample surface. The energy loss of the ions in this scattering process is dependent on the mass of the surface atom it was scattered from. The peaks in the energy spectrum of the backscattered ions are used to identify and quantify the elemental composition of the outer surface.

Ions that are scattered in deeper atomic layers are first of all efficiently neutralized and lose energy by nuclear and electronic stopping on their way through the sample. This causes a shift in energy proportional to the distance traveled in the solid, and a lower intensity of those ions. Due to this, the scattering from the first atomic layer can be distinguished from sub-surface scattering, leading to the extreme surface sensitivity of just one atomic layer [1].

However, even ions scattered below the surface can be detected if the surface promotes the reionization of neutralized primary ions after their travel through sub-surface layers. This can be used to determine layer thickness and elemental distribution in the first few nm of the sample in a fast and non-destructive measurement. The required stopping power values are calculated using SRIM [2].

In this study we applied LEIS to a range of samples of ALD deposited Pd on Al_2O_3 substrates. The currently used process for the Pd deposition requires high temperatures to facilitate the desorption of residuals from the Pd precursor, which poison the substrate surface and inhibit the further nucleation of Pd. This leads to island growth of Pd clusters. We demonstrate how LEIS can be used to analyze the surface coverage of the deposited Pd, the Pd cluster dimensions, and the amount of precursor residual. This information is crucial to develop a lower temperature process for the deposition on temperature sensitive substrates, such as polymers.

[1] Surface composition analysis by low-energy ion scattering, Brongersma, H. H.; Draxler et al., Surf Sci Reports, 62, 2007, 63-109

[2] The Stopping and Range of Ions in Solids (Pergamon, New York, 1985)

AS-TuP8 Real-time Monitoring of Surface Reactions by Means of Cluster-induced Desorption/Ionization Mass Spectrometry*, A. Portz,* Justus Liebig University Giessen, Germany*; **ChristophR. Gebhardt**,* Bruker Daltonics Bremen, Germany*; M. Durr,* Justus Liebig University Giessen, Germany

The reactions of biomolecules on surfaces are of great interest both from a fundamental point of view as well as with respect to applications such as surface functionalization. However, the chemical information obtained by standard surface analysis tools is limited. Recently, we have shown that desorption/ionization induced by neutral clusters (DINeC) is a soft and matrix-free ion source for mass spectrometry of biomolecules. DINeC employs molecular clusters of 10^3 to 10^4 SO_2 molecules; the clusters do not only provide the energy necessary for desorption but, due to the high dipole moment of SO_2, also serve as a transient matrix in which the desorbing molecule is dissolved during cluster-surface impact. Thus desorption takes place at comparably low cluster energies (< 1eV/molecule); shattering of the clusters during and after surface impact furthermore leads to a rapid redistribution of the system's energy. As a consequence, desorption takes place without fragmentation of the desorbing molecules.

In this contribution, we demonstrate that DINeC can be used for real-time monitoring of surface reactions of larger molecules such as porphyrins and oligo-peptides. The quantitative nature of the method was demonstrated using angiotensin II molecules individually adsorbed on gold substrates by means of electrospray ion-beam deposition. These adsorbates were desorbed and detected as intact molecules down to a coverage of 10^{-13} mol/cm^2 (0.001 ML); a linear relationship between surface coverage and signal intensity was observed over three orders of magnitude. Real-time monitoring of surface reactions is demonstrated for isotope-exchange experiments with angiotensin II and different types of porphyrins. Dosing D_2O led to a broadening of the isotopic pattern and a continuous shift towards higher m/z values. When the D_2O pressure was chosen high enough, the H/D exchange rate was determined by the exchange process itself. The results were modeled by means of Monte Carlo simulations taking into account reaction and back-reaction of H/D exchange. Several different rate constants could be extracted and are assigned to the different types of functional groups in the respective molecules.

AS-TuP9 Improved X-ray Photoelectron Spectroscopy Analysis using the PHI *VersaProbe* III*, **Jennifer Mann**, J.S. Hammond, J.F. Moulder, B. Schmidt,* Physical Electronics USA

Based on its proven scanning X-ray Photoelectron Spectroscopy (XPS) microprobe core technology, Physical Electronics has introduced the newest version of its *VersaProbe* product line; the *VersaProbe* III. Multiple improvements over the *VersaProbe* II model have been incorporated into this new design including:

1. Higher sensitivity for all analysis areas
2. Increased number of detector channels for faster imaging
3. Collection angle defining aperture for angle dependent studies
4. Improved hot/cold stage temperature range
5. Dedicated high temperature mount for increased temperature experiments
6. Dedicated 4-contact sample mount for in-situ controlled potential experiments

This poster will discuss these improvements in more detail and show examples where they are beneficial in XPS experiments.

AS-TuP10 Multiple Technique Investigation of UV-grafted Polymers*, **Lopamudra Das**, M.J. Kelley,* College of William and Mary

The major increased-value opportunities for polyesters depend on affordable, environmentally-friendly surface modification. We report the use of 172 nm UV light to induce surface radicals that offer graft sites for desirable functionalities on PET, PTT, PBT and PEN. Obtaining insight into the mechanisms and results requires multiple techniques, notably XPS, ToF-SIMS, AFM and FTIR.

AS-TuP11 Analysis of Thin Phase-Shifter Films using Surface Analysis Techniques*, **Vincent Smentkowski**,* General Electric Global Research Center*; L. Le Tarte,* GGeneral Electric Global Research Center*; H. Piao,* General Electric Global Research Center*; M. Marko,* Wadsworth Center

Many types of phase-shifters have been developed for use in place of the TEM objective aperture. The phase shifters act to increase phase contrast by providing high transfer of information over a very wide spatial-frequency range. Unfortunately, many of these devices fail shortly after being installed into the instrument due to charging in the electron beam, so we have been experimenting with surface deposition of novel thin-film metals. In some cases, it is essential that the electron-scattering cross-section of the metal film be as small as possible, so the films must often be quite thin (less than 10 nm thick). Accurate analysis of such thin films is required to understand the composition of the layers, unexpected impurities both in the films and at the interfaces, the oxidation state of the layers, and the lateral uniformity of the layers.

In this poster we use a suite of surface analysis techniques to monitor the distribution of species through one multilayer phase plate stack comprised of 2nm Rh, 6nm C, and 2nm Al using depth profiling protocol. The pros and cons of each of the surface analysis techniques are illustrated via the sample analyzed. Each of the three techniques used here were able to successfully identify and resolve each of the 3 layers with a sufficient number of data points defining the thin layers. Each of the techniques also revealed oxygen in the aluminum layer with a stoichiometry of about Al_2O_3.

An advantage of ToF-SIMS for depth profiling is the ability to rapidly collect an image at every depth, allowing for 3D rendering of the data sets. The 3D ToF-SIMS renderings do not reveal discontinuous regions at a length scale of a few hundred nm (the conditions used here); ruling out holes at a length scale of less than a few hundred nanometers in the Rh layer would require ToF-SIMS analysis using a pulsing mode with a smaller analytical spot size. Another advantage of ToF-SIMS is that a full mass spectrum is saved at every voxel and hence all elements and high mass molecular fragments are analyzed. Often unexpected species are revealed sub surface. A disadvantage of ToF-SIMS is the ion yield varies depending on the composition of the matrix and this makes quantitative analysis more difficult. In contrast sensitivity factors have been developed for both AES and XPS and these reported sensitivity factors are typically valid to within 10% and hence quantitative analysis is easier.

Mike Marco acknowledges funding through NIH grant GM103555.

AS-TuP12 Improving the Performance of the Cylindrical Mirror Analyzer by Electrode Segmentation*, David Edwards, Jr,* IJL Research Center

Electrode segmentation of the cylindrical mirror analyzer has been shown to significantly improve the resolution of the standard instrument. The high precision solution which had been found for the 42.3 device is shown in this report to exist in fact for an extended set of input angles or equivalently for a range of sample positions. This has allowed a significant limitation of the CMA, namely the critical dependence of instrument performance on sample position, to be largely overcome. In addition by placing the sample at the minimum in the curve of resolution vs sample position, a resolution of ~.000045 has been obtained for a +-6 degree bundle an improvement of a factor of ~40 over the standard spectrometer. Thus electrode segmentation has been found not only to significantly improve the device performance, but in fact to enable its high precision to be realized.

AS-TuP15 Impact of Surface Contaminants on ToF-SIMS analysis of Wood Polymer Composites (WPCs)*, Laura D. Brunelle, Z.A. Gernold, C.S. Swagler, E.R. Welton, R.E. Goacher,* Niagara University

Wood Polymer Composites (WPCs) are a promising material for outdoor applications, such as decking and marine structures, because they have improved properties over wood or plastic alone. WPCs also allow for the recycling of plastics and use of reclaimed wood. However, the use of WPCs poses questions regarding the breakdown and weathering of WPCs. The importance of the interface between wood and polymer components of the composite may make analysis with a chemical imaging technique such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) advantageous. Due to the high surface sensitivity of ToF-SIMS, an understanding of the surface contaminants on WPCs is required. Contaminants on WPCs may arise from handling, storage, or from lubricants and other components used in the manufacturing process. As such, even new material surfaces can be considered contaminated. Therefore, the interiors of the WPCs were used as references, as the interior is an unhandled surface. The removal of contaminants by solvents (including purified water, isopropyl alcohol, and mixtures thereof) was evaluated to identify appropriate cleaning methods. Furthermore, it may be desirable to remove contaminants prior to or after controlled weathering experiments. Therefore, the chosen cleaning method was applied to previously weathered samples. Comparisons of ToF-SIMS spectra of the WPCs were performed using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR). This work provides insight into how the surface and interior of the WPCs differ, how treatment with common solvents alter the obtained spectra, and how weathered surfaces appear with and without cleaning.

AS-TuP16 Examining the General Applicability of ToF-SIMS for Wood Polymer Composite (WPC) Analysis*, Christopher S. Swagler, L.D. Brunelle, M.R. Michienzi, E.R. Welton, R.E. Goacher,* Niagara University

The interface between hydrophobic plastic and hydrophilic wood in Wood Polymer Composites (WPCs) is important for the strength and durability of the materials. WPCs are used in decking and marine structures because they have improved properties over wood or plastic alone. WPCs are relatively new materials and prior research into their weathering and durability has focused on the issue of interface adhesion. Such studies have used Scanning Electron Microscopy (SEM) for morphological analysis, and many have included chemical analysis using X-ray Photoelectron Spectroscopy (XPS). However, XPS has poor imaging resolution and only provides elemental and functional group analysis. For a more detailed analysis of the wood-plastic interface, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) offers higher imaging resolution than XPS, and can provide more detailed molecular information. To date, ToF-SIMS analysis of WPCs has been limited to preliminary studies involving the weathering and cleaning of a single commercially available product. These analyses have shown ToF-SIMS to have promise for the analysis of weathering, using spectral, imaging, and depth profiling approaches. The present study expands this analysis to include a wider variety of sample types, such as those made from polypropylene, nylon or styrene maleic anhydride plastics, with and without added dyes. The composition of these samples is better known than the composition of the previously analyzed commercial material, which aids in identification of peaks from the polymer, wood, and any additives. The analysis of a wider set of unweathered WPCs provides baseline information about the observable chemical distributions for comparison to weathered samples. ToF-SIMS results are also compared to visual light microscopy, SEM, and XPS to illustrate complementarity with these techniques. This work provides insight into how the ToF-SIMS spectra and images vary for WPCs of different composition, including new and reclaimed materials.

AS-TuP17 Swift Heavy Ion Irradiation for Designing Planar Field Emitters and Exchange Bias Layers*, Debalaya Sarker*[*]*, S. Bhattacharya,* Indian Institute of Technology Delhi, India*; S. Ghosh, P. Srivastava,* Indian Institute of Technology Delhi

In this talk, I shall give a brief overview of engineering ferromagnetic metal-insulator (FM_M/SiO_2 FM_M=FeCo, Ni) nano-composites having application in device physics. Increasing demand of flat displays necessitates to design planar emitters which not only miniaturize the device but also have several other advantages like mechanical durability, temporal stability etc. FM_M nanoparticles (NPs) inside SiO_2 matrix, when subjected to Swift Heavy Ion (SHI) irradiations get elongated. Using this, we demonstrate here a planar field emitter with maximum current density of 550 $\mu A/cm^2$ at an applied field of 15 V/μm. The film, irradiated with 5×10^{13} ions/cm^2 fluence (5e13) of 120 MeV Au^{9+} ions, shows very high electron emitting quantum efficiency in comparison to its unirradiated counterpart. We find experimental evidence of enhanced valence band (VB) density of states (DOS) for 5e13 film from XPS, which is further verified in the electronic structure of a model FM_M cluster from combined density functional theory (DFT) and *ab initio* molecular dynamics (MD) simulations. The MD temperature is taken from the lattice temperature profile from thermal spike model. Increasing the SHI fluence beyond 5e13, results in reduced VB DOS and melting of surface protrusions, thus causing reduction of FE current density. We finally conclude from DFT that change in fluence alters the co-ordination chemistry followed by the charge distribution and spin alignment, which influence the VB DOS and concurrent FE as evident from our experiment.[1,2] More recently, we have explored the effect of shape and structural anisotropies on magnetic properties of SHI irradiated FM_M/SiO_2 flims. Magnetic anisotropy (MA) and exchange bias effect (EBE) were tuned by monitoring SHI irradiation fluence. The in-plane and out-of-plane M-H loops show that the perpendicular MA reaches a maximum value at 5e13 and then decreases. At highest fluence an EBE is observed. Underlying electronic structure was not only probed with XANES and XPS VB, but also is validated from our non-collinear theoretical calculations. We conclude this EBE is an outcome of formation of anti-ferromagnetic domains due to spin-flipping at high temperature. In summary, elongated FM_M NPs inside SiO_2 matrix are designed using controlled SHI irradiation. Due to its high current density and mechanical/chemical durability, the irradiated films open new possibilities for the development of electronic displays. They also show sufficient promise in magnetic storage media for their interesting MA and EBE properties.

Reference:

[1]D. Sarker *et al.*, ACS Appl. Mater. Interfaces, 8, 4994 (2016).

[2]D. Sarker *et al.*, J. Appl. Phys, 115, 174304 (2014).

AS-TuP18 Improving Relative Quantitation in Imaging Lipidomics using ToF-SIMS*, Marwa Munem, J.S. Fletcher,* University of Gothenburg, Sweden

Introduction

ToF-SIMS is of increasing value to clinicians and has been used on a number of tissue samples to successfully identify and localise different chemical components to various areas of the tissue and answer disease related questions [1]. Compared to traditional histology or fluorescence staining, the main advantage of ToF-SIMS is the label free detection of a large number of different molecules simultaneously on the same tissue section. New gas cluster ion beams (GCIBs) provides benefits for imaging larger molecular species [2]. These improvements still leave issues such as greatly varying ionisation efficiencies for different molecules and matrix effects. In

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[*] **National Student Award Finalist**

some biological samples changes in Na or K concentration through the sample can lead to different pseudo-molecular ions being preferentially generated from different parts of the sample.

Methods

A J105 ToF-SIMS instrument (Ionoptika Ltd, UK) was used to analyse salt adduct effects on lipids ionization by exposing different standard lipids and tissue samples to different concentrations of sodium and potassium salts mixtures. Tissue sections from mouse heart, rat brain and cancer biopsy samples were imaged on the same instrument adduct formation assessed.

Results

In positive ion mode the relative intensity of $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$ ions from phospatidylcholine phospholipids changes dramatically with just a small change in in the Na:K ratio in the sample. The situation is further complicated by changes in relative intensities of fragment ions. The ratio of the $[M+Na-59]^+$ to the $[M+Na]^+$ peak is significantly smaller than the equivalent ratio from potassium adduct ions. Using these different peaks corrected images of different lipids can be generated from images of tissue sections obtained by ToF-SIMS.

Conclusions

Matrix effects, in this case variation in salt content in biological samples, can lead to difficulties in (relative) quantitation of different biological species. The changes in ionisation and fragmentation observed in ToF-SIMS measurements show similar trends to those observed with other mass spectrometry methods where adduct formation is used as a tool for influencing fragmentation in tandem MS experiments[3].

[1] David Toubel, Sandrine Roy, Dominique P. Germain et al., *Int. J. Mass Spectrom.* 2007, 260(2-3), 158-165, Sjövall Peter, Björn Johansson et.al., *App. Surf. Sci*, 2008, 255 (4), 1177–1180, Michael A. Robinson, Daniel J. Graham, Fionnuala Morrish et al., *Biotinterphases*, 2016, 11, 02A303

[2] T. B. Angerer, P. Blenkinsopp, J. S. Fletcher, *Int. J. Mass Spectrom.* 2015, 377, 591-598

[3] Rian L. Griffiths and Josephine Bunch, *Rapid Commun. Mass Spectrom.* 2012, 26, 1557–1566

AS-TuP19 XPS Investigation of UHP Mg and Mg Alloys Exposed to Water: Peak Fitting the Mg 2p Core Level Spectra to Distinguish Oxide from Hydroxide*, **Harry Meyer**, D. Leonard, M.P. Brady,* Oak Ridge National Laboratory

Magnesium alloys are increasingly used in structural materials applications requiring high strength and light weight. Alloys containing Mg are also of interest in biomedical applications (implants) and energy materials applications (fuel cells, batteries, and hydrogen storage). The Department of Energy has aggressive materials research projects aimed at increasing the use of magnesium and magnesium-based alloys for vehicle applications. The primary interest in vehicles is to reduce the overall vehicle weight by substituting lighter weight Mg-alloys. One of the primary obstacles for increased use of Mg-alloys is the corrosion behavior of these materials. Oak Ridge National Laboratory has been studying aqueous corrosion behavior for several years to try to develop an understanding of the carrion film formation mechanism. The material presented in this poster is a portion of that larger program and is focused on using x-ray photoelectron spectroscopy (XPS) to study Mg-alloy corrosion. In this study we have exposed four Mg materials (UHP Mg; Mg-0.27Zr; Mg-0.14Nd; and Mg-2Al) to water for 4 hours to elucidate early film formation. Ar-ion depth profiling was used to compare the thickness of the corrosion films and to try to understand the partitioning between oxide and hydroxide growth. This poster demonstrates the Mg 2p peak fitting strategy that was employed. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-TuP20 Root-Cause Analysis of an Interfacial Adhesive Failure Based on Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)*, **James Ohlhausen**, P. Vianco,* Sandia National Laboratories

Low Temperature Co-fired Ceramic (LTTC) substrates are used for high frequency electronics assemblies. The LTCC material is comprised of alumina particles in a silica-based, glassy phase; the latter also includes Na, Mg and Ca oxides. The surface conductor traces and pads are a Au/Pt/Cu/Ti metallization where Ti is the adhesion layer. Delamination was experienced at the interface between the Ti layer and LTCC. Determining a root-cause to the delamination was made difficult by the complexity of the LTCC material and air exposure of the test samples before being introduced into the vacuum chamber for surface analysis. This air exposure of already de-adhered interfaces potentially compromises the cleanliness of the mutual, interface surfaces due to oxidation and adventitious contamination that caused significant challenge for the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) assessment.

ToF-SIMS was used to analyze the de-adhered interfaces as well as to evaluate the unexposed interface by means of the depth profile mode. The ToF-SIMS tool was able to identify key Pb, Na, K, and Ca markers that confirmed the widespread coverage of the surface by the glassy phase. The role of organic contamination was similarly documented at the de-adhesion sites. The data obtained from these ToF-SIMS assessments confirmed that delamination was caused primarily by the propensity of the glassy phase to cover the LTCC surface. Small variations to the glass phase composition accounted for the intermittent presence of delamination. This poster will outline the specific ToF-SIMS test steps as well as the data analysis and methodologies that allowed for a conclusion to be developed for the delamination event.

**Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-TuP21 Surface and Bulk Property Studies of Newly Developed High Performance Transparent Conductor Material*, **Lei Zhang**, W. Wu, N.G. Tassi, D. Walls,* DuPont Science and Engineering

Nowadays, transparent conductor (TC) materials have been widely applied into various areas including displays such as LCD & OLED, touchscreens, and photovoltaics. While indium tin oxide (ITO) has been used as a dominant TC material, due to the rareness of indium metal, scientists have been working to develop new/alternative TC materials to meet special needs in different application areas.

In the area for large touch screen panel application, copper mesh material can be a good TC candidate because of Cu's high electrical conductivity and low material cost. However, Cu is unstable in air and easily forms Cu(I)/Cu(II) oxides, plus Cu atoms are easily diffused to other layers in the devices to cause device malfunctioning. To stabilize the Cu surfaces, graphene is selectively deposited on the surfaces of the micro-grids by atmospheric pressure chemical vapor deposition (CVD) method. Integrated analytical techniques including X-ray photoelectron spectroscopy (XPS), Raman, and others were applied to characterize the surface, bulk, and electrical properties of the graphene coated Cu/Ni micro-grid systems. Results indicated the realization of long-term stability of the new TC structure. This presentation will cover the development and study of this high performance and stable graphene coated copper/nickel micro-grids transparent conducting structure.

AS-TuP22 Optimizing the Surface of Perovskite Oxide/Carbon Composites as Catalysts for the Oxygen Reduction Reaction in Alkaline Media*, **Michael Dzara**, C. Ngo,* Colorado School of Mines*; J. Christ,* National Renewable Energy Laboratory*; P. Joghee, C. Cadigan, T. Batson, R. Richards, R. O'Hayre, S. Pylypenko,* Colorado School of Mines

Developing non-precious metal catalyst (NPMC) materials for the oxygen reduction reaction (ORR) is a critical research area in order to drive the widespread commercial adoption of low temperature fuel cells. Current technology uses Pt or other precious metal-based catalysts; by replacing these expensive precious metals with inexpensive, earth-abundant NPMCs, the economic feasibility of low temperature fuel cells can be significantly improved. However, improvements in the performance of NPMCs are needed in order to compete with precious metal-based catalysts. Perovskite oxide structures (ABO_3)are one of the candidates among themany materials being evaluated as NPMCs for the ORR in alkaline media. Many elements can form perovskite oxide structures that are stable in alkaline media, and the properties of these structures can be tuned by doping the A and B sites, providing an extremely vast range of possible structures to explore.[1] Performance of perovskite oxides has been shown to improve by creating a perovskite oxide/carbon composite, as carbon improves the conductivity of the composite and has an active role in catalyzing the ORR.[2] However, like other NPMC chemistries perovskite oxides are heterogeneous by nature, and it is therefore difficult to correlate material properties with catalytic performance.

Here, our work focuses on understanding the interplay of surface chemistry and surface morphology of $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides and their composites with carbon. An aerogel synthesis method was used to produce $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides with surface areas from approximately 5-80 m^2/g. By varying synthesis parameters, materials with different surface chemistry and morphology were produced. Detailed characterization of surface composition and morphology are performed using physisorption, x-ray photoelectron spectroscopy, and transmission electron microscopy equipped with energy dispersive X-ray spectroscopy. This information is correlated to rotating ring-disk electrode electrochemical measurements in alkaline media. These techniques help provide understanding of the surface properties of $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides and their impact on performance, providing a path towards optimization of the surface chemistry and morphology for improved catalytic performance.

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**AS-TuP23 Tuning of N-Doping in Carbon Nanospheres for Investigation of Catalyst-Support Interactions*, Matthew Strand,* *C. Ngo, A. White, J. Hagen, S. Pylypenko,* Colorado School of Mines

Continued increase of worldwide energy consumption necessitates the development of renewable energy resources. Fuel cells can utilize a wide variety of renewable fuels, but poor long term stability of the catalyst impacts their economic viability. High surface area carbon is utilized as a state-of-the-art catalyst support, and research has shown that the presence of dopants such as nitrogen can improve the stability of catalyst nanoparticles.[1,2] The interplay between nitrogen concentration, graphiticity, and specific nitrogen functionalities and their effect on catalyst-support interactions is still not well understood. Such investigations require the use of model high-surface area materials and multi-technique characterization approach.

In this work, a series of nitrogen-doped carbons was created to serve as model high-surface area substrates with the goal to: investigate in more detail the effect of nitrogen and specific nitrogen functionalities on the stability of metal nanoparticles; enable in situ microscopy analysis of catalyst-support interactions; and serve as a platform for atomistic analysis of dopants in high-surface area carbon materials. N-doped carbon nanospheres were synthesized using a previously published sol-gel method,[3] varying both the amount of nitrogen precursor and pyrolysis temperature in order to vary nitrogen concentration and speciation. Samples were first characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to determine nanosphere sizes, then by nitrogen physisorption for surface area and porosity analysis. Detailed analysis with Raman and X-ray photoelectron spectroscopies was completed to correlate changes to the parameter space of the synthesis with ratio of amorphous to graphitic carbon, relative concentrations of nitrogen, and different nitrogen functionalities.

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AS-TuP24 Electron Microscopy Study of Fission Product Migration in Irradiated TRISO Nuclear Fuel*, Rachel Seibert,* Illinois Institute of Technology*; C. Parish, P. Edmondson, K. Terrani,* Oak Ridge National Laboratory*; J. Terry,* Illinois Institute of Technology

High temperature gas cooled reactors (HTGRs) may use tristructural-isotropic (TRISO) coated nuclear fuel particles. Fuel performance is limited by the interaction of fission products with the barrier SiC layer. In particular, Ag is released from intact TRISO fuel, and Pd may locally corrode the SiC. Additionally, uranium and plutonium migration are of interest. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors. We have studied TRISO particles produced at ORNL under the Advanced Gas Reactor fuel program. The fuel was irradiated at the Advanced Test Reactor at Idaho National Laboratory. The local chemical structure of three TRISO SiC shells was examined through X-ray absorption fine structure spectroscopy (XAFS) at the Materials Research Collaborative Access beamline at the Advanced Photon Source. To complement these results, electron microscopy studies have been conducted on various samples prepared from these SiC fragments at the Low Activation Materials Development and Analysis (LAMDA) facility at ORNL. Specifically, samples were prepared from the inner, outer, and middle interfaces of the SiC fragment to obtain a full cross-sectional image of the fission product migration. These results have provided key information on the fission product transport behavior through irradiated SiC at varying temperatures. Knowledge of these reaction pathways will allow for better simulation of the long-term behavior of TRISO fuels. They may also suggest ways to modify the SiC layer to improve fuel performance and mitigate fission product release, which is critical for safety strategies required to commercialize HTGRs.

AS-TuP26 X-ray Photoelectron Spectroscopy Analysis of Titanium Nitride-Nickel Nanocomposite Catalyst*, Samuel Gage,* Colorado School of Mines*; V. Molinari, D. Esposito,* Max Planck Institute of Colloids and Interfaces, Germany*; S. Pylypenko,* Colorado School of Mines

Titanium nitride-nickel (TiN-Ni) nanocomposites have been recently found to be an efficient catalyst for the hydrogenolysis of aryl ethers as models for lignin biomass refining. As compared to Ni catalysts supported on carbon, TiN-Ni nanocomposites showed superior catalytic activity. One possible explanation for the improved performance is a change in the electronic structure of nickel due to the TiN support. In order to test this hypothesis, a series of TiN-Ni nanocomposites with varying amounts of Ni loadings (1, 10, 20 and 50 wt.%) were synthesized and investigated using X-ray Photoelectron spectroscopy (XPS) and microscopy techniques. A series of TiO_2-Ni reference materials with identical Ni loadings served as a reference.

The binding energy of Ni in the TiN-Ni samples is higher than those measured for Ni supported on TiO_2, indicating that Ni in TiN-Ni nanocomposites is more electron poor. At Ni loadings greater than 1 wt.%, higher concentrations of Ni were measured on the surface of the TiN support as compared to the TiO_2 support. The increase in the Ni loading appears to preferentially block TiN surface sites. In contrast at 1 wt.% loadings, the amount of Ni detected on the surface of TiN support is lower than that observed on the surface of TiO_2 support, suggesting incorporation of Ni into the TiN structure.

AS-TuP27 Redox Active Cerium Oxide Immobilized on Highly Ordered Polymer Nanopillars as Dopamine Sensor*, Swetha Barkam*[*]*,* *M. Peppler, S. Das, S. Saraf, C. Li, J. Thomas, S. Seal,* University of Central Florida

Dopamine, is one of the main neurotransmitters which plays a significant role in the function of human metabolism, hormonal, cardiovascular and central nervous systems. Several diseases and neurological disorders such as Parkinson's disease, schizophrenia and Huntington's disease can be caused due to deficiency of dopamine. Therefore lower concentration detection of dopamine in biological samples such as sweat and/or urine containing dopamine metabolites is very crucial. In this study, we propose cerium oxide coated polymer nanopillars based sensor to achieve lower limit detection of dopamine with high sensitivity and selectivity for diagnostic applications. Cerium oxide nanoconstructs (nanoceria) that have the potential to act as antioxidant attributed to its switching of oxidation state from +3 to +4 mediated at the oxygen vacancies. The unique inter action between dopamine and the redox active nanoceria is studied using *in-situ* UV-visible spectro-electrochemistry and surface characterization methods. It has been previously observed that there is a strong attachment of dopamine to nanoceria surface through oxidation followed by formation of a charge transfer complex, there by motivating to develop a sensor to detect dopamine. In this study, cerium oxide is immobilized on high aspect ratio nano-pillars made of polyacrylonitrile polymer. The nanopillars fabricated using soft lithography increased the surface area of exposed cerium oxide, thereby increasing the interaction of the nanoparticles with dopamine. The changes in the redox potential and surface chemistry of cerium oxide coating upon reaction with dopamine were recorded using electrochemical and optical techniques. Cerium oxide coatings were obtained using different techniques such as sputter coating, atomic layer deposition, electrodeposition and spin coating to obtained different surface chemistry (ratio of Ce^{3+}:Ce^{4+} on the surface) to improve the detection limit of the dopamine.

AS-TuP28 X-ray Photoelectron Spectroscopy of Raw Material for Metal Additive Manufacturing*, David Wieliczka,* *A.S. Choi, J.A. Crow, C.J. Cook, L.F. Elder, R.D. Koch, T.A. Pond, B.C. Sartin, D.R. Shinault, S.E. Van Slyke,* Honeywell Federal Manufacturing and Technology

Understanding the effects of powder reuse on metallurgical properties of components fabricated via laser powder bed fusion is critical to ensure the production of functional components. The inability to reuse metal AM powder will have a significant negative economic impact on this manufacturing method. In mid-2015, the KC NSC initiated a 316L powder

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[*] **National Student Award Finalist**

study on a consistent run of components. This paper will present surface analysis results from both virgin metal powder and powder sampled from the overflow bin after a build. In addition to XPS, the powders have been examined with SEM/EDS to provide morphology and composition, direct probe mass spectroscopy to examine the outgassing of the material, and ICP-MS to examine the impurities at ppm levels. The XPS data was obtained from the surface of the powder as well as a function of depth utilizing argon ion sputtering and provides unique information on the elemental composition of the surface. Specifically, we were tracking the elemental surface enrichment due to vapor created during the build process. We are also examining the oxide chemistry of both the surface and near surface region.

AS-TuP29 Characterization of Bonding between Super-hard Ceramics and Polymer Substrate*, **Ranganathan Parthasarathy**,* Tennessee State University*; JB. Beam,* Vanderbilt University*; FEH. Hoff,* Tennessee State University*; A. Misra,* University of Kansas*; L.Z. Ouyang,* Tennessee State University*; CML. Lukehart,* Vanderbilt University

Superhard coatings improve the durability of biomedical polymer implants due to their excellent wear resistance. We study the bond strength between Rhenium Diboride (ReB_2), a superhard ceramic, and Teflon, which is widely used as an implant material in load-bearing biomedical applications. As part of a proof-of-concept study, ReB_2 is coated onto Teflon using confined-plume chemical deposition at room temperature and pressure. For the coating to function effectively in load-bearing conditions, the bond strength between the polymer and the coating must well exceed in-situ stresses. Accurate local measurement of bond strength using nano-indentation is difficult owing to platelet microstructure of the ReB_2; hence an experimental workflow was designed to determine the average macro-scale bond strength between Teflon substrate and ReB_2 coating. The inert nature of Teflon makes conventional pull-out challenging. Therefore, we performed a)Tensile pull-out of the deposited ceramic coating based on a modified version of ASTM D4541, b) Imaging of failure surfaces using light microscopy and Scanning Electron Microscopy (SEM) c) Image segmentation to determine area of failure, and d) Calculation of average stress at pull-out. The tests reveal average bond strength of 2.5 MPa between Teflon and ReB_2 for coatings deposited on an untreated Teflon surface and 4.5 MPa for those on a sanded and etched Teflon surface. The pull-out occurs in a brittle manner, with no observable yield or plastic flow. The SEM images reveal strands of Teflon on the pull-out side, indicating that the true bond strength is likely higher than the measured average. Imaging of the Teflon surface under the coating reveals that the confined-plume chemical deposition creates a laminate surface of ReB_2 on the substrate, as opposed to anchored platelets. The results confirm the development of a robust and repeatable workflow for the measurement of average bond strengths of super-hard ceramic coatings on comparatively soft polymer substrates.

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