Applied Surface Science
Room: Hall 3 - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP1 Applications of EMSL's Radiochemistry Annex (RadEMSL) in Understanding of the Chemical Fate and Transport of Radionuclides in Terrestrial and Subsurface Ecosystems, ***Mark Engelhard***, Pacific Northwest National Laboratory

(RadEMSL) is a radiochemistry facility, which is part of EMSL, Environmental Molecular Sciences Laboratory, a Department of Energy Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at PNNL. This facility is designed to accelerate scientific discovery and deepen the understanding of the chemical fate and transport of radionuclides in terrestrial and subsurface ecosystems. In this poster we present results obtained from two different studies that have utilized the X-ray Photoelectron Spectroscopy (XPS) capability in this facility.

The first application involved XPS analysis of Uraninite (UO_2). UO_2 is the primary component of most nuclear fuels, and can be a major phase in bio-remediated uranium- contaminated soils and aquifers. Understanding the mechanisms of UO_2 surface oxidation and corrosion is essential to predicting its stability in the environment throughout the nuclear fuel cycle. XPS shows clear evidence of U(IV) and U(V) oxidation states consistent with computational results. This new mechanism may be relevant to other fluorite structures, including plutonium dioxide (PuO_2).

The second application involves XPS analysis of Np. Neptunium (Np) is a long-lived radionuclide environmental contaminant associated with weapons production and processing that is transported in the subsurface as actinyl NpO_2^+. The radioactive metallic element Np is created when uranium-based nuclear fuel is burned up in electricity-producing commercial reactors and in plutonium-producing reactors operated for military purposes. Researchers examined factors that impact structural incorporation of Np(V) neptunyl and U(VI) uranyl ions into carbonate and sulfate minerals. Co-precipitation of Np(V) into mineral structures could reduce transport in the subsurface and shows promise as a groundwater remediation strategy.

Rad(EMSL) offers experimental and computational tools uniquely suited for actinide chemistry studies. The spectroscopic and imaging instruments at this facility are ideally designed for the study of contaminated environmental materials, examination of radionuclide speciation and detection of chemical signatures. The annex houses nuclear magnetic resonance instruments and surface science capabilities, such as X-ray photoelectron spectroscopy, electron microscopy, electron microprobe, transmission electron microscopy and scanning electron microscopy.

AS-ThP2 XPS and AES Characterization of Tribofilm Formation on Non-Metallic Coatings Using ZDDP and Ionic Liquid Lubricant Additives, ***Harry Meyer III***, *J. Qu, Z.B. Cai, C. Ma, H. Luo*, Oak Ridge National Laboratory

Interactions between oil additives and non-metallic surfaces are less well understood than tribofilm formation on metallic surfaces. The most common anti-wear additive for metallic surfaces is zinc dialkyldithiophosphate (ZDDP). In this study, ZDDP and a phosphonium–organophosphate ionic liquid (IL) are used with three hard coatings (AlMgB14– TiB2, TiB2, and diamond like carbon), to determine what, if any, tribofilms are formed when sliding against a steel ball. Systematic characterization was conducted on the coating wear scars including top surface morphology imaging and elemental mapping, layer-by-layer chemical analysis, and cross section nanostructural examination. For boride coatings, tribofilms formed by ZDDP+IL are up to 50-70 nm thick with 75-80% surface coverage. On the other hand, tribofilms on DLC were <25 nm thick and only covered 20-30% of the contact area. The presence of iron compounds in the tribofilms suggests a critical role for wear debris in tribofilm formation. In addition, oxidation products of TiB_2 were detected in the tribofilms. No involvement of the DLC surface in tribofilm formation was observed. Results suggest that wear debris digestion and contact surface reaction both are critical in tribofilm formation: the former process is responsible in forming the bulk of the tribofilm and the latter provides strong bonding of the tribofilm to the contact surface. In this poster, the emphasis will be how scanning Auger microanalysis and x-ray photoelectron spectroscopy were used for characterizing the ZDDP+IL-derived tribofilms.

AS-ThP3 XPS Sputter Depth Profiling of Organometallic Multilayer Materials using Massive Argon Cluster Ions, ***Simon Hutton***, Kratos Analytical Limited, UK, *T. Bendikov*, Weizmann Institute of Science, Israel, *W. Boxford, S.C. Page, J.D.P. Counsell, A.J. Roberts, C.J. Blomfield, S.J. Coultas*, Kratos Analytical Limited, UK

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) have revolutionised the study of such organic thin films by depth profiling with techniques such as X-ray photoelectron spectroscopy (XPS). As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.

In this study we present results from GCIS XPS depth profiling of 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. [1] The layer-by-layer deposition approach used here allows multiple building blocks to be incorporated into the film.

Depth profiling through the films using the GCIS allowed the structure to be confirmed and relative layer thicknesses to be tentatively compared. The depth profiles were carried out using optimised conditions for cluster formation and X-ray exposure was limited to reduce detrimental effects, including modification of the etch rate, noted elsewhere. [2]

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[2] P. Cumpson, J. F. Portoles, N. Sano, and A. J. Barlow, *J. Vac. Sci. Technol. B* 31(2), 2013.

AS-ThP4 XPS Analysis and Sample Preparation for EBSD Analysis using Argon Gas Clusters, ***Adam Bushell***, Thermo Fisher Scientific, UK, *R. Simpson*, University of Surrey, UK, *C.J. Stephens, C. Deeks, T.S. Nunney, J.P.W. Treacy*, Thermo Fisher Scientific, UK

The use of noble gas ions for sputter cleaning and profiling materials in X-ray Photoelectron Spectroscopy (XPS) analyses is well established. Monatomic ions are generally used while analysing hard inorganic materials, providing efficient cleaning and a good sputter rate while profiling. More recently, argon ion clusters have been found to be very effective at cleaning and profiling organic materials. Cluster ion sputtering of these materials is suitable for cleaning the surface without inducing chemical modification, but it also has potential for preparing surfaces for analysis by techniques other than XPS.

In this presentation we will show the results of an investigation into using a range of cluster energies and sizes not only for XPS, but how they can be used for sample preparation in EBSD. We will illustrate the potential level of successful EBSD analysis that can be achieved when the appropriate etching criteria are used on a sample.

AS-ThP5 Comprehensive Characterization High-k Dielectric Films Deposited by ALD using Multi-Technique Surface Analysis, ***Richard White***, Thermo Fisher Scientific, UK

It has been known for many years that XPS is the ideal technique for characterizing ultra thin layers encountered during semiconductor device fabrication. Standard XPS analysis allows the analyst to detect and quantify elements and chemical bonding states in the stack of layers within 5-10nm thickness. Extension of the analysis to angle resolved XPS (ARXPS) adds another dimension to the data, enabling non-destructive depth profiling of the stack and the measurement of buried layer thickness.

Modern XPS spectrometers, which also come pre-configured with additional surface analysis techniques, can measure several other parameters of interest to the semiconductor engineer/scientist. As well as measuring surface elemental and chemical state information, XPS can provide the analyst with electronic information such as band gap and valence band offset. The complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) can also give a measurement of band gap in those situations where XPS has trouble, e.g. when the stack contains hafnium oxide.

Finally, if an XPS spectrometer is also configured with Ion Scattering Spectroscopy (ISS) then a direct indication of film surface coverage can be made. This technique measures the kinetic energy of noble gas ions

scattered from a surface and can be used to investigate the growth mode of high-k films during atomic layer deposition.

AS-ThP6 XPS and ToF-SIMS Characterization Functionalized 3D Mesostructures fabricated by Direct Laser Writing, ***Michael Bruns**, A. Welle, A.S. Quick, T. Claus, G. Delaittre,* Karlsruhe Institute of Technology, Germany, *T.S. Nunney,* Thermo Fisher Scientific, UK, *M. Wegener, C. Barner-Kowollik*, Karlsruhe Institute of Technology, Germany

In recent years significant effort has been spent to develop strategies for the fabrication of structured (bio)polymer modified surfaces on various substrates to alter the properties or to introduce entities with specific functions. These still ongoing activities are mainly stimulated by the wide range of applications in various scientific fields, such as lab-on-a-chip technology, biointerfaces, and tissue engineering. The utilization of photo-triggered Diels-Alder reactions in combination with shadow masking is an established efficient tool to achieve precise chemically structured surfaces in 2D.[1, 2] However, when aiming at the fabrication of complex 3D structures equipped with different surface functionalities, direct laser writing (DLW) is the method of choice. Most recently developed photoresists comprising e.g. orthogonal thiol-yne chemistry and click chemistry for a subsequent dual surface modification open up a facile avenue to fabricate various structures with several tailored functionalities.[3] In all cases surface analytical methods are indispensable to prove the successful chemical modification in a non-destructive manner. Therefore, the present contribution focuses on the characterization of such 3D structures using the combination of X-ray photoelectron spectroscopy (XPS) and complementary time-of-flight secondary ion mass spectrometry (ToF-SIMS). For non-patterned samples XPS quantitatively evidences the successful functionalization of surfaces for every single reaction step, whereas ToF-SIMS allows for rapid investigation of the chemical 2D patterning at high spatial resolution. For selected samples advanced parallel XPS imaging is additionally applied to calibrate the ToF-SIMS findings, obtaining quantitative information. For the chemical surface characterization of the well-defined 3D structures, ToF-SIMS proves an efficient tool for non-destructive 3D characterization of excellent spatial resolution with the advantage to achieve chemical/molecular information simultaneously.

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[3] A. S. Quick, A. de los Santos Pereira, M. Bruns, T. Bückmann, C. Rodriguez-Emmenegger, M. Wegener and C. Barner-Kowollik, Adv. Funct. Mat. 2015, in press.

This work was carried out with the support of the KNMF, a Helmholtz Research Infrastructure at KIT.

AS-ThP7 Structure, Surface Analysis, Photoluminescent Properties and Decay Characteristics of Tb^{3+}-Eu^{3+} Co-Activated $Sr_2MgSi_2O_7$ Phosphor, *M.A. Tshabalala, O.M. Ntwaeaborwa,* University of the Free State, South Africa, ***Simon Dhlamini***, University of South Africa

Strontium magnesium silicate ($Sr_2MgSi_2O_7$) is an alkaline earth silicate that belongs to a group of natural minerals of the melilites group called sorosilicates. Sorosilicates have the same basic crystal structure and they can be represented by a general formula $A_2MT_2O_7$ (A = Ca, Sr, Na; M = Mg; and T = Si, Al, B)[1]. They usually crystalize in a tetragonal structure with a space group $P42_1m$. Due to their tetragonal crystal structure without an inversion center, lanthanides or transition metals can be incorporated easily as activators or dopants in melilite hosts[2]. Due to this ease of incorporation, melilites are today widely used as host lattices for rare-earth dopant and transitional metal ions to prepare light emitting materials or phosphors that can be used in many practical applications such as flat panel displays, light emitting diodes, solar cells and many other types of light emitting devices. In this study, we investigated the structure, chemical and electronic states, ionic and atomic distribution and photoluminescent properties of $Sr_2MgSi_2O_7$ single doped with Eu^{3+} or Tb^{3+} or co-doped with Eu^{3+} and Tb^{3+} by a solid-state reaction method. It turned out that the emission color could be tuned from blue to green or white depending on the dopant concentrations and the excitation wavelength.

The structure, stretching vibrations, chemical and electronic states, and photoluminescent properties were studied using X-ray powder diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Time-of-flight secondary ion mass spectrometer (TOF-SIMS) and Photoluminescence (PL) spectroscopy respectively. The XRD pattern of the $Sr_2MgSi_2O_7$:Eu^{3+}, Tb^{3+} phosphor resemble the standard tetragonal phase of $Sr_2MgSi_2O_7$. The fitted XPS data demonstrated that there were two different Sr^{2+} sites in the host lattice and a site occupied by Mg^+ cations which connects the Sr^+ sites with the Si^+ ions. The TOF-SIMS results demonstrated localization and distribution of various ions within the host lattice (Sr_2MgSiO_7) including the Tb^{3+} and Eu^{3+} dopants. The photoluminescence data indicated that the emission colour could be tuned from blue-green depending on the concentration of Tb^{3+}. The white photoluminescence was observed from the Tb^{3+}-Eu^{3+} co-activated system. This tunable emission has potential application in solid state lighting like white and multicolor light emitting diodes (LEDs).

References

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AS-ThP8 XPS Study of Many-Electron Interaction & Exchange Interaction of Local Moments in Ion Beam Synthesized Ternary Transition Metal Silicides, ***Wickramaarachchige Lakshantha**, M. Dhoubhadel, F. McDaniel, B. Rout*, University of North Texas

In recent years, the interest in ternary metal (iron) silicides system is triggered by its potential use in advanced silicon based opto-electronic devices. However the ternary silicides have been by far less studied than their binary counterparts despite the fact that they might be beneficial in decreasing the formation temperature of disilicides. The phase formation of ternary silicides is not well understood, because most often the ternary silicides are formed in metastable phases. Among the well-known synthesis techniques to form or modify the composition and physical properties of thin films, low energy ion implantation has shown to be a very powerful technique. The ternary metal silicides can be synthesized by sequentially implantation of two metals into a Si substrate. In this study, Fe-Co-Si & Fe-Ti-Si ternary phases were formed by sequentially implanting either Co or Ti, along with Fe into Si (100) at room temperature (RT). Dynamic ion implantation simulation was performed to determine the ion fluences for concentration saturation of implant ions in the Si matrix. Then the optimal saturation fluences of each ions were implanted at 50 keV into Si substrates. Further same implantation process were performed under an externally applied magnetic field. The samples were subsequently annealing at temperature ranging from 200 – 600 ºC. X-ray diffraction (XRD) analysis shows that even without annealing significant amount of ternary phase formation for ion implantation under external magnetic field. Further structural evolutions of ternary phases were observed with the annealing temperature. X-ray photoelectron spectra show core-level (Fe $2p_{3/2}$ & 3s) spectral asymmetry and splitting in these transition metal compounds. We believe this is the direct evidence of high Density of State (DOS) at valance band and a local moment in the ternary compounds.

AS-ThP9 Using ToF-SIMS to Characterize Surface Contamination in Sandia's Z Machine, ***James Ohlhausen**, B. Clark, R. Tang, D. Lamppa, D. Susan, R. Sorensen*, Sandia National Laboratories

The Z machine at Sandia National Laboratories is the world's most powerful and efficient laboratory X-ray radiation source. It generates 3-MV, 100-ns, 20-MA current pulses to compress target loads and produce high temperatures, high pressures, and 300-TW X-ray pulses for research in high energy density science. The Z machine target is fed by four parallel Magnetically-Insulated Transmission Lines (MITLs). The MITLs and target load hardware must be located in a high-vacuum chamber because of the exceptionally high electric- and magnetic-field stresses. The MITL electrode surfaces must be as clean as possible to maximize current delivery to the load. Residue from hardware handling, post-shot debris, and other environmental contaminants may generate electrode plasmas that contribute to current losses exceeding 6 MA for certain types of loads. Decreases in current delivery negatively affect all aspects of Z shot performance.

This analysis is part of a larger experiment to evaluate the efficacy of *in-situ* plasma cleaning within the Z machine's load region. Witness samples taken from different steps during hardware preparation and installation are used to characterize surface contaminants. ToF-SIMS is uniquely suited to perform analysis of these surfaces owing to its ability to image large areas while measuring elemental and chemical information. Both organic and inorganic species were detected in the form of particles and films. Contaminants found during the Z machine load hardware lifecycle were characterized before and after plasma cleaning to determine the effectiveness of plasma processing on the specific contaminants found. Methods of acquisition, analysis and quantification will be shown. Preliminary findings from the ToF-SIMS analysis will be presented.

**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-ThP10 Going Beyond Visualization: Exploiting Synergies Between Electron Microscopy and ToF-SIMS, ***Kathryn Lloyd****, C.D. Chan, J.R. Marsh, D.J. Walls, S. Subramoney*, DuPont Corporate Center for Analytical Sciences

As is most often the case with research and development characterization challenges, no one analytical technique is able to "tell the complete story". The combination of inorganic and organic layers and components in today's advanced materials and display systems requires new sample preparation and analytical strategies. Natural systems such as leaves and seeds, as well as hair and skin, require molecularly specificity. A common analytical need is to be able to distinguish phases or layers at sub-micron lateral resolution, based on molecular signatures.

Electron microscopy (SEM or TEM) is often the first step towards sub-micron visualization. ToF-SIMS (secondary ion mass spectrometry) provides mass spectral data, and thus molecular specificity, with typically 1 micron lateral resolution. Since the lateral resolution of EDS, often used in conjunction with SEM to provide elemental maps, is also around 1 micron, the two techniques can be combined with the secondary electron images to provide a more complete chemical picture. Organic contamination in metal powder synthesis and feed granule coatings provide two examples.

Cross-sectional sample preparation using Focused Ion Beam (FIB) technology has allowed SEM and TEM visualization of layers and defects that could not be achieved using more traditional sample preparation approaches. A companion analysis for these types of samples is top-down ToF-SIMS depth profiling, as the depth resolution in this type of experiment is typically tens of nanometers or less. Combining the information from these two approaches is challenging and not always straightforward. Examples from displays and other layered structures will be shown.

AS-ThP11 The Benefits of Using All of the Measured Mass Channels During MVSA of ToF-SIMS Data Sets, ***Vincent Smentkowski****,* General Electric Global Research Center*, M.R. Keenan,* Independent Scientist*, H. Arlinghaus*, ION-TOF GmbH

Time of flight secondary ion mass spectrometry (ToF-SIMS) data sets are very large and contain a wealth of information about the material being analyzed. A typical image data set can be comprised of 256 x 256 pixels with a 0 to 900 amu (or greater) mass spectrum collected at high ($M/\Delta M$ ~10,000) mass resolution at every pixel. Data sets are often comprised of >1 x 10^{15} spectral channels. The challenge for a ToF-SIMS analyst is to scrutinize all of the measured information without bias in order to provide for the most robust understanding of the material being analyzed; this is especially important in an industrial setting where unknown samples are analyzed. Multivariate statistical analysis (MVSA) algorithms have assisted in ToF-SIMS data work up [1,2], however commercially available software is not able to handle data sets this large and the analysts often select mass intervals to utilize and/or degrades the mass resolution prior to MVSA analysis. In this poster, we will report first results obtained using MVSA software that is able to handle massive ToF-SIMS data sets. We demonstrate two important benefits of unbiased analysis of the massive ToF-SIMS data sets: (1) finding unexpected elements in real world samples (this is a reason why the authors never use peak lists for MVSA analysis) and (2) the ability to obtain high mass resolution results from data sets collected at nominal mass resolution (e.g., the beam alignment pulsing mode on ION-TOF instruments). The importance of these two benefits will be highlighted.

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[2] Surface and Interface Analysis, Special issue on Multivariate Analysis II. Volume 41 issue 8, Aug 2009

AS-ThP12 Electron Gun Tilting and Shifting with O-Ring Stack System, ***In-Yong Park****, B. Cho,* KRISS, Korea*, C. Han,* KBSI, Korea*, D. Lee, S.J. Ahn*, KRISS, Korea

Most of the charged particle instruments (CPBIs) have the gun which generates a charge particle beam and column which controls a beam direction. In CPBIs, the precise alignment between gun and column is very important to get a best performance, such as high imaging resolution and patterning resolution. Generally, mechanical moving and electro-magnetic deflection are adopted to adjust beam path relatively in the each component. Most mechanical alignment operations use sliding single O-ring or thin metal bellows, which allow motion while preserving the internal vacuum. However, single O-ring allows the only small changes of shifting and tilting. For the double-deflector, an electronic part controlling the applied voltage or current is necessary, a fairly difficulty to assemble double-deflector part inside a vacuum chamber included. In this work, we center around on a simple and cheap electron gun alignment method in the laboratory experiment and early stages of CPBIs development.

To monitor the electron beam movement controlled by flange motion, we use a thermionic electron source and maintained a vacuum pressure of approximately 10^{-5} Pa with a combination of a rotary pump and a turbo-molecular pump which ran in tandem. In order to accelerate the generated electron beam, the electron gun system is floated at a negative 20 kV and the filament is heated by adjusting the current flow. Finally, the accelerated electrons hit the phosphor screen and make the visible light. We stacked ten O-rings and insert the metal center rings between O-rings to maintain the structure stably. We assembled four identical structures, all of which can shift the gun flange vertically and horizontally with clamping screws and separate it azimuthally with an equal space on the flange, which is under the O-rings. We monitored the beam position at the phosphor screen in real time shifting and tilting the flange on which electron gun is installed. Also, we get the nearly identical values comparing the experiment result and theoretical calculation result. This means that we can control the electron beam direction precisely with O-ring stack system maintaining the inside vacuum pressure steadily. We demonstrate a tilting angle of ±2.55° with shifts of ±2 mm experimentally[1], values which are generally sufficient for application to CPBI gun alignment, as this adjustable range can cover the error range when the parts are made and assembled. It can also be applied when insulation is needed between the flanges while maintaining some degree of freedom.

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AS-ThP13 Covalent Surface Modification of Silicon Oxide Substrate using Aliphatic Alcohols and Microwave Radiation, ***Austin Lee****, B.D. Gates*, Simon Fraser University, Canada

Microwave radiation is used to react alcohols with silicon oxide surfaces to form self-assembled monolayers (SAMs). Advantages of using alcohols as building blocks for the formation of SAMs include their widespread availability, ease of handling, and stability against side reactions. Challenges to preparing monolayers of aliphatic alcohols on silicon oxide surfaces include the relatively high temperatures and slow reaction kinetics of the alcohol condensation reaction. Microwave radiation delivers sufficient thermal energy for the condensation reaction to occur in a fast, efficient manner. To demonstrate this capability, monolayers of 1-butanol, 1-octanol, and 1-octadecanol were successfully formed with the assistance of a microwave oven, and the monolayers were evaluated using Soxhlet extraction, WCA, AFM, and XPS. We optimized this reaction to render the silicon oxide surfaces hydrophobic, and successfully coated alcohols onto both the native oxide of silicon substrates and glass microscope slides.

AS-ThP16 XPS Analysis of Polycrystalline Samples $(Bi_3M)(Sb_3M)O_{14}$ type Pyrochlore with M = Cu, Co and Zn, ***Lazaro Huerta****, R. Escamilla, M. Romero,* Universidad Nacional Autonoma de Mexico*, M. Flores,* Universidad de Guadalajara, Mexico*, A. Duran*, Universidad Nacional Autonoma de Mexico

The general formula of the oxide pyrochlores can be written as $A_2B_2O_6O'$ with four crystallographically nonequivalent atom sites. These compounds have potential applications in a variety of applications as catalysis, magnetic and ionic conducting materials. A particular pyrochlore-type phase with $Bi_{1.5}ZnSb_{1.5}O_7$ stoichiometry is used in ZnO-based varistors, a polyphasic ceramic with property based on the grain boundary phenomenon. Here, we synthetized the polycrystalline samples of $(Bi_3M)(Sb_3M)O_{14}$ with M = Cu, Co and Zn by solid state reaction. The samples were characterized by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. X-ray diffraction studies revealed that the *a* lattice parameter increases with Cu, Co and Zn respectively. On the other hand, the Cu 2p, Co 2p, Zn 2p, Bi 4f and O1s core levels were analysed and the valence bands respective were studied.

AS-ThP17 XPS Analysis of CN_x Thin Films, ***Niklas Hellgren***, Messiah College*, R. Haasch,* University of Illinois at Urbana-Champaign*, S. Schmidt, L. Hultman,* Linköping University, Sweden*, I. Petrov*, University of Illinois at Urbana-Champaign

X-ray photoelectron spectroscopy (XPS) has for decades been one of the most widely used techniques for analyzing the quantity and bonding states of nitrogen in carbon-nitride compounds, in particular hard carbon-nitride films in wear-protective applications, and more recently for analyzing nitrogen doping states in graphene used for electronic applications. Interpretation of the C1s and N1s spectra, however, can be very challenging due to the many possible bonding configurations of N and C, combined with the inevitable interaction with oxygen and hydrogen on the film surface. A corresponding debate over interpretation has accompanied the field.

In this study we report on XPS studies of magnetron sputtered CN_x thin films, with x ranging from ~0.1 to 0.6. Different growth conditions result in films of different structures, from amorphous to graphite-like and fullerene-

like. In order to address some of the above-mentioned difficulties, films were analyzed by angular-resolved XPS, first *in-situ* in the growth and analysis chamber, then after air exposure, and finally after Ar ion etching using ion energies ranging from 500 eV to 4 keV.

The as-deposited films typically exhibit two strong N1s peaks at ~398-398.5eV (usually assigned to pyridine-like nitrogen, C–N=C), and ~400-400.7eV (graphitic nitrogen, –N<), with some nitrile contribution (–C≡N) in between, at ~399eV. Interestingly, the in-situ spectra also show a shoulder in the 402-404 eV range, which is typically attributed to oxidized nitrogen (N-O). However, this peak does not increase upon air exposure, which shows that a different assignment is required for this peak. Instead, air exposure results in the gap between the two main peaks being filled, presumably due to an increase in pyrrole-like nitrogen (>N-H) and/or amino-like nitrogen (>NH_2). Meanwhile, the C1s peak broadens on the high-energy side which indicates that the 5-10 at.% oxygen uptake on the film surface is primarily in the form of C-O and possibly H_2O, but not N-O.

Argon ion etching readily removes surface oxygen, but also results in a strong preferential sputtering of nitrogen. The N/C ratios rapidly approach equilibria of 0.05-0.2, depending on the initial concentration and the Ar^+ beam energy. Furthermore, changes in the N1s peak shape indicate that ion etching causes amorphization of the film surface. Both effects are more pronounced at higher ion energies, and the damage does not appear to be reversible with subsequent low-energy etching. The best methods for evaluating the as-deposited film structure and composition with *ex-situ* XPS will be discussed.

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Treacy, J.P.W.: AS-ThP4, 1
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Walls, D.J.: AS-ThP10, 3
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