Applied Surface Science Division
Room On Demand - Session AS-Contributed On Demand
Applied Surface Science Contributed On Demand Session

AS-Contributed On Demand-1 Peeling the Onion: Argon Cluster Sputtering Reveals the Internal Distribution of Species in Organic Nanoparticles*, Y. Pei, J. Vorng, R. Havelund, D. Cant,* ***Alexander Shard,*** National Physical Laboratory, UK

Ideally, we would like to get detailed structural information from nanoparticles and sub-micrometre particles by removing each layer of material and analysing the freshly exposed surface, like peeling an onion. Trying to do this using traditional surface analysis methods is difficult enough to make anyone cry, also like peeling an onion. However, if we could approach this, the quantitative power and molecular specificity of XPS and SIMS would be invaluable to the development of functional organic particles, such as those used in drug delivery and diagnostic applications. By sputtering monodisperse sub-micrometre polystyrene particles with an argon cluster ion beam we demonstrate that their shape can be usefully modelled using a constant, angle-independent sputtering yield. This permits the development of a model to analyse XPS and SIMS data from surfaces coated with multilayers of monodisperse PTFE-PMMA core-shell particles. In this work, the SIMS data shows clear peaks for the fluorinated core signal from at least three layers of the packed particles, demonstrating potentially useful information. The XPS data from the first layer of particles can be analysed using our model to establish the diameter of the core which agrees, to within 6%, with SEM measurements of the uncoated core. Furthermore, the internal distribution of PTFE agrees with the expected distribution of internal core locations, which is an equally weighted random distribution, with no part of the core closer than ~10 nm of the surface. Whilst the SIMS data is potentially more useful for material identification, it implies a core diameter 40% smaller than expected and more closely located at the centre of the particle. We show that this discrepancy is most likely due to a SIMS matrix effect in which PMMA suppresses the generation of positive secondary ions from PTFE.

AS-Contributed On Demand-4 Buried Interface and Buried Film Analysis Using Lab-Scale Haxpes Instruments*,* ***Thierry Conard****, C. Zborowski, A. Vanleenhove, I. Hoflijk, I. Vaesen, P. van der Heide,* IMEC, Belgium

Nanotechnology is playing a fundamental role in the improvement of our life conditions. Progress in various domains such as microelectronics, storing and producing energy (batteries, solar cells, ...) and life sciences is very often linked to the improvement of our knowledge about interactions at material interfaces. Photoemission has a major role in the characterization of surfaces and interfaces thanks to its wide availability in laboratories all over the world. However, traditionally, the photon energy is limited since standard photoemission lab-tools were equipped with soft X-ray Mg Kα or AlKα radiation (~1.5 keV), which makes the analysis of buried interfaces deeper than a few nanometers impossible without the use of destructive profiling methods (sputtering), leading to strong chemical modification of the layers/interfaces analyzed.

Unfortunately, in many modern technologies, deeper interfaces need to be analyzed. This can be done by increasing the photon energy. However, until recently, this has seldomly been applied as it required synchrotron radiation, which was only available in specialized synchrotron facilities with limited access while process development usually requires a fast feedback loop and routine measurements. However, the recent development of several lab-scale instruments including high photon energy monochromatized sources (Ag Kα ~2.9keV, Cr Kα ~5.4 keV or Ga Kα ~9.25 keV)opened the possibility of non-destructive buried interface analysis for process development work.

In this presentation, we will demonstrate the possibilities of the HAXPES lab-scale systems from Physical Electronics (PHI*Quantes*, using Cr Kαphotons) and ScientaOmicron (*HAXPES-lab*, using for Ga Kα photons) for two different applications. First, we will look into the chemical analysis of interfaces in multi-layer high-k/metal gate stacks (such as $TiN/HfO_2/SiO_2Si$) and investigate the modifications of the layer chemistry of the buried layers upon thermal treatments. One of the difficulties in using concomitantly Al Ka-based and high-energy photoemission is achieving coherent quantification. Therefore, the second part of the presentation will describe an approach by which the necessary sensitivity factors are determined. The resulting quantification accuracy will be demonstrated by a quantitative analysis of the composition of binary and ternary materials (such as InAs, InGaAs, InGaZnO, ...).

AS-Contributed On Demand-7 ***Non-Destructive Chemical Characterization and Thickness Determination of Layer Stacks by Laboratory-Based Hard X-Ray Photoelectron Spectroscopy , Anja Vanleenhove,*** *T. Conard, C. Zborowski, I. Hoflijk, P. van der Heide,* IMEC, Belgium*; K. Artyushkova, D. Watson,* Physical Electronics USA

XPS is widely used for non-destructive analysis of the chemical composition of thin layers and interfaces. In its angle-resolved mode, it can be used for the determination of composition depth profiles and layer thicknesses. With the commonly used soft X-ray laboratory instrument, the analysis is limited to the top 5-10nm. The recent development of laboratory-based hard X-ray photoelectron spectroscopy with an X-ray energy higher than 5keV opens the opportunity to examine layers and interfaces buried up to 20nm and deeper in a non-destructive way. To evaluate the application of lab-based HAXPES for thickness and composition determination, various multilayer samples with total thicknesses up to 20nm are examined by HAXPES and soft X-ray XPS. All experiments are performed in a PHI Quantes system equipped with two monochromatic X-ray sources, Al Kα (1486.6eV) and Cr Kα (5414.7eV), hence combining both XPS and HAXPES in one instrument.

Both angle resolved and angle integrated data analysis options are discussed. In the first part, we discuss the analysis of angle resolved data, resulting in relative depth profiles and thickness information, which is performed with the MultiPak and StrataPHI software. The latter is recently developed by Physical Electronics, USA. We discuss the analysis with regard to instrumental parameters and the physical parameters (attenuation lengths, sensitivity factors, etc.) necessary for the calculations. In a second part, we demonstrate how the analysis of angle integrated spectra can provide identical information by combining XPS and HAXPES data, thus eliminating the need to perform time-consuming angle resolved measurements.

The samples considered in this study – multilayer Al_2O_3 and HfO_2, SiO_2, Si_3N_4, ZrO_2, ZnO, Lu_2O_3, TiN – originated from semiconductor processing. The thin film multilayer stacks, which are within the range of both XPS and HAXPES sampling depth, are examined both by XPS and HAXPES. The results are validated by HAADF-STEM and EDS analysis. The thicker stacks are used to demonstrate the specific interest of HAXPES for increased depth-information capabilities.

AS-Contributed On Demand-10 Temperature Dependent Changes in Surface Chemistry of $SrTiO_3$ Analysed With XPS, Cluster Depth Profiling and Ion Scattering Spectroscopy*,* ***Paul Mack,*** Thermo Fisher Scientific, UK

Small cluster (Ar_{300}^+) depth profiling of a $SrTiO_3$ thin film has previously been demonstrated.Compared to low energy (500eV) monatomic argon sputtering, the cluster depth profiling caused much lower chemical damage, with a more realistic [Sr]:[Ti] stoichiometry observed throughout the profile and lower chemical damage to the Ti^{4+} oxidation state.$SrTiO_3$ is of interest because it has potential use in energy storage or photocatalysis and if future devices performance is to be optimized, it is necessary to accurately measure film compostion/chemistry and also to understand how these may change when the devices are exposed to changes in local conditions, such as temperature.

In an extension to previous work, a $SrTiO_3$ sample has been analysed with XPS cluster depth profiling over a range of temperatures (from room temperature to >600°C).One of the aims of the work is detect reduction of the Ti^{4+} oxidation state to Ti^{3+}, caused by changes in temperature.The chemical shift in the Ti2p region is reasonably large (~2eV), but the relative concentration of any Ti^{3+} formed can be quite low.Distinguishing the Ti^{3+} from the Ti^{4+} therefore requites the XPS system to have very high sensitivity and good charge compensation.

Additionally, ion scattering spectroscopy (ISS) was used to evaluate the termination of the $SrTiO_3$ film as a function of temperature.ISS is even more surface sensitive than XPS and is the ideal analytical technique for measuring if there are local changes in the top monolayer of the $SrTiO_3$, e.g. -TiO_2 termination.Combination of small argon cluster profiling with both XPS and ISS gives a more comprehensive characterization of the $SrTiO_3$ than is possible with just a single analytical technique.

AS-Contributed On Demand-13 LiTaO$_3$(110) Nano-Bonding with Si-based Materials via Surface Energy Engineering (SEE) and Three Liquid Contact Angle Analysis (3LCAA)*, **Shefali Prakash**, A. Elison, S. Swaminathan, M. Sahal,* Arizona State University*; B. Baker, J. Kintz,* Intel Corporation*; A. Yano,* Texas A&M University*; S. Narayan,* University of Pennsylvania*; A. Brimhall,* Micron Technology*; L. Puglisi, R. Culbertson, N. Herbots,* Arizona State University

Integrating piezo-electrics to Si can be achieved by Direct Wafer Bonding (DWB) for materials with large mismatch in lattice constant and/or Coefficients of Thermal Expansion (CTE).

DWB by Nano-Bonding™ uses SEE instead of high temperature is a logical choice for bonding LiTaO$_3$ to Si and SiO$_2$, since the CTE of LiTaO$_3$(110), ~18.3 × 10^{-6}/K, is mismatched to Si by a factor 8, and to α-quartz SiO$_2$, (α-q SiO$_2$) by a factor 25. Moreover, at 500 K, LiTaO$_3$ decomposes into Ta$_2$O$_5$ and Li.

Surface Energy Engineering (SEE) for Nano-Bonding™[1] modifies the Surface Energy, γ^T, and hydro-affinity, HA, to far-from-equilibrium states, in air, planarizes at the nano-, micro- and macro-scale, and nucleates *2D-Precursor Phases*, in synergy for both materials. 2D precursor phases act as catalysts when in contact, forming a cross-bonded, solid *interphase*. To engineer γ^T and HA, the initial γ^T of as received wafers is computed from the Lifshitz-van der Waals' interaction energy, γ^{LW}, acceptors energy, γ^-, and donors energy, γ^+, measured using Three Liquid Contact Angle Analysis and the van Oss–Chaudhury–Good theory.

B-doped p^--Si(100) is uniformly hydrophilic with a water contact angle θ_{H20} of 37.7 ± 0.6°[2]. 6" α-q SiO$_2$(100) is uniformly hydrophilic, with a θ_{H20} of 65.5 ± 0.6°. LiTaO$_3$(110) is mostly hydrophobic, with an average θ_{H20} of 49.4 ± 6.6°, and poor uniformity across 6"[3]. Hydrophilic α-q SiO$_2$(100) γ^T averages 48.7 ± 1.5 mJ/m^2. γ^T averages 40.8 ± 2 mJ/m^2 for LiTaO$_3$ (110), and 53 ± 0.2 mJ/m^2 for Si(100).

The ΔG of interaction for LiTaO$_3$ (110) with Si(100) is -8.18 mJ/m^2 and -0.46 mJ/m^2 with α-q SiO$_2$, at RT in atmosphere and HR = 25%. The negative signs of ΔG reveal that spontaneous bonding between LiTaO$_3$(110), and Si(100) and α-q SiO$_2$(100) is energetically favored.

Hence, LiTaO$_3$(110) and Si(100) could spontaneously nano-bond when nano-contacted at RT, which is in fact observed experimentally[2]. SEE can lower the ΔG to enhance the kinetics of Nano-Bonding™ interphase formation and bonding strength. Ab-Initio Molecular Dynamics (MD) simulations of LiTaO$_3$(110) Surface Density of State (DOS) simulation using CrystalMaker® for LiTaO$_3$(110) in contact with Si(100) before and after SEE can yield insights into the engineering of ΔG, by correlating computed modified surface charges, maximized dipole moments, electronic configuration to the measured γ^T.

[1] US & Int. Pat. 6,613,677; 7,851,365;9,018,077;9,589,801 (2017)

[2] Baker, B. *et al*.,J. of Vac.Sci& Techn.A37, no. 4 (2019): 041101

[3] Sahal, M.*et al*. Bull.of the APS 64 (2019)

AS-Contributed On Demand-16 Understanding *Interphase* Formation in Nano-Bonding™ Of Gaas to Si in Air at T ≤ 220°C via Surface Energy Engineering Based on 3lCAA, IBA, XPS, SAM and TEM*, A. Gurijala, N. Suresh, A. Chow, S. Khanna, M. Sahal,* Arizona State University Physics Department*; S. Ram,* Yale University*; T. Diaz, M. Bertram, C. Cornejo, W. Peng, T. Balasooriya, T. Karcher,* Arizona State University Physics Department*; R. Culbertson,* Arizona State University Physics Department*; K. Kavanaugh,* Simon Fraser University, Canada*; N. Herbots,* Arizona State University Physics Department*; **Pranav Penmatcha**, S. Jandhyala,* Arizona State University

Si and GaAs absorb the solar spectrum between 0.4 -1.1 µm and 0.8 - 2 µm with a PV Conversion Efficiency (PVCE) ~ 24%, and ~ 35 %, respectively. Integrating GaAs to Si yields more efficient tandem cells. However, their PVCE reaches presently only ~ 33 %[1].

DWB by Nano-Bonding™[1-3](NB) in air uses Surface Energy Engineering (SEE) to remove native oxide, shift surface energies, γ^T, and hydro-affinity (H-A) far-from-equilibrium, planarize surfaces by reducing warp and roughness, and form *2D Precursor Phases*[2-4](2D-PP) to catalyze molecular cross-bonds via electron exchange. NB activates 2DPP to form a cross-bonding *interphase* under 35-60 kPA and/or gas pressurization. 2DPP formation is described in [2].

$\gamma^T$and H-A are measured by Three Liquid Contact Angle Analysis to ± 1 mJ./m^2 from contact angles for water, glycerin, and α-bromonaphthalene. Ion Beam Analysis via nuclear resonance with channeling measures O coverage to ± 0.2 - 0.5 ML. X-Ray Photoelectron Spectroscopy analyzes composition and bonding.

As-received (AR) Te-doped n+-GaAs is hydrophobic, with γ^T = 33 ± 1 mJ/m^2. After SEE, GaAs becomes *super-hydrophilic*with γ^Tdoubling to 66 ±1 mJ/m^2. Meanwhile, AR B-doped p^--Si[3-4] is initially hydrophilic with γ^T = 53 ± 1mJ/m^2, and becomes hydrophobic after SEE with γ^T = 48 ± 3 mJ/m^2. Absolute Oxygen coverage decreases on n+-GaAs from 7.2 ± 0.5 ML to 3.6 ± 0.2 ML, and from 13.3 ± 0.5 ML to 11.8 ± 0.5 ML on Si p^--Si .

The As$_2$O$_5$to As$_2$O$_3$ ratio decreases by a factor 2. So the same amount of As is bound to Oxygen, but to three O rather than five.

The GaAs to Ga$_2$O$_3$ ratio remains 6:4. Adventitious C affects XPS data by < 10% with a correlation factor < 0.6.

SEE reverses hydro-affinity of Si and GaAs without affecting the Ga:As ratio.

The GaAs/Si interface is imaged by Surface Acoustic wave Microscopy (SAM) and cross-section TEM. 98% of the compressed GaAs area to Si is found bonded, when using 40 kPa and steam pressurization. In addition, the cross-bonding is found to extend beyond the compressed area into the regions around it where mechanical compression is not applied. The additional surface area found to be bonded can reach up to 8 times the compressed area.

The reaction rate is estimated from X-TEM. Key parameters to maximize bonding, and the mechanism of cross-bonding *interphase* formation during NB of GaAs to Si in air are derived from experiments varying SEE and NB conditions and will be discussed.

1. NREL, 2020.
2. Int. US Pat. 6,613,677; 7,851,365; 9,018,077; 9,589,801 Herbots *et al.*
3. Ram S *et al.* **MRS Adv.** 4, 41-42 (2019): 2249-2263.
4. Cornejo, C E. *et al.*, **MRS Adv.** 3, 57-58 (2018): 3403-3411

AS-Contributed On Demand-19 Computed Surface Vibration Modes, IR Absorption and Gibbs Free Energy for LiTaO3(110) and LiNbO3(110) Correlation with Surface Energies Measured via 3LCAA*, **Mohammed Sahal**, A. Elison, S. Prakash, S. Swaminathan, R. Rane, L. Puglisi, B. Baker, R. Culbertson, N. Herbots,* Arizona State University

Piezoelectric LiTaO$_3$(LT) and LiNbO$_3$(LN) monolithic integration to Si has the potential to deliver IC's with infrared and acoustic sensing capabilities.

The lattice mismatch of LT(110) and LN(110) with Si(100) is almost identical, ~ 34%, and ~ 48% with α-q SiO$_2$(100). Such large mismatch limits hetero-epitaxy of relaxed LT and LN on Si. Moreover, deposition involving multiple buffer interface layers is difficult due to thermal instability of both LT and LN above 500K, which decomposes into Ta or Nb oxides while Li$^+$ out-diffuses.

Nano-Bonding™(NB[4]), a Direct Wafer Bonding (DWB) process carried out in a Class 10/ISO 4 environment aims to form molecular cross-bonds at the interface of two distinct wafers via a distinct ordered inter-phase[1,2] Room Temperature NB uses Surface Energy Engineering (SEE) to eliminate three key issues with DWB and hetero-epitaxy: lattice mismatch, Coefficient of Thermal Expansion mismatch and thermal instability.

SEE modifies the initial equilibrium state of surfaces into a metastable 'far-from- equilibrium' state via nano-scale planarization, and causes the nucleation of 2D-Precursor Phases[3,4,5]. 2D-PP can be activated at room temperature by gas and mechanical pressurization to form molecular cross-bonds. Design of SEE for a material pair involves surface energy γ and hydro-affinity H-A measurement via Three Liquid Contact Angle Analysis (3LCAA) using the van-Oss-Chaudhury-Good theory followed by γ modification of 6'' wafer surface into a 'far-from-equilibrium' meta-stable state.

In this work, γ components and ΔG_{H20} measured on 'As Received' (AR) LT(110), LN(110), α-q SiO$_2$(100) and Si(100) are inter-compared with their computed IR absorption spectra, Surface Electron Density of States(SE-DOS) simulated by Crystal Maker®.

The highest IR Spectrum Intensity Peaks(IRS-IP)was observed for α-q SiO$_2$(100) with a wavenumber of 1330 cm^{-1} with a Polar Surface Energy (PSE) value as 14 ± 1.3 mJ/m^2. Similarly, IRS-IP for LT(110), LN(110) and

Si(100) were 1014 cm^{-1}, 1278 cm^{-1} and 489 cm^{-1} and their PSE contributions were 4.7 ± 0.2 mJ/m^2, 7.5 ± 2.1 mJ/m^2 and 5 ± 0.4 mJ/m^2 respectively. IRS-IP simulated on each wafer STL were representative of their respective PSE contributions since PSE contributions decreases with higher order of surface symmetry. It should be noted that the PSE of LT(110) is slightly lower than Si(100), which could be due the presence of Si(100) native oxide. Wafers having IRS-IPs, PSE contributions had least symmetric SE-DOS as expected. These results lay the foundation to correlate and predict the macro-thermodynamic γ components and Gibbs free energy change with their atomistic models and simulations.

AS-Contributed On Demand-22 Quantitative Fabric Analysis of Clay Flocs Using Two-Dimensional X-Ray Diffraction*, Tao Jiang,* *G. Zhang,* UMass Amherst

Clay flocs, by definition, are groups of clay particles associated primarily with face-to-face association to form structural units in clays via small-scale surface/interfacial forces. Owing to the widespread presence of clay minerals in the terrestrial and marine environments, understanding the microstructural characteristics of clay flocs is crucial in many environmental process and industrial applications. In this study, two-dimensional X-ray diffraction technique was employed to yield quantitative analysis of clay flocs. A group of pure kaolinite flocs with concentration of 1 g/l were first absorbed into a Kapton tube, and then subjected to the transmission of X-ray generated at MIT X-ray diffraction shared experimental facility. After multiple frames of scanning with varying tilt and rotation angles, pole figure that represent the stereographic projection of the orientation of crystal planes. The results indicate that the kaolinite floc group has random particle orientation when no external load is applied.

AS-Contributed On Demand-25 Deep Depth profiling using Gas Cluster SIMS – Micrometer Topography Development and Effects on Depth Resolution*, Shin Muramoto,* NIST*; D. Graham,* University of Washington

Secondary ion mass spectrometry using the argon cluster primary ion beam enables molecular compositional depth profiling of organic thin films with minimal loss of chemical information or changes in sputter rate. However, for depth profiles of thicker organic films (> 10 µm of sputtered depth) we have observed the rapid formation of micron-scale topography in the shape of pillars that significantly affect both the linearity of the sputter yield and depth resolution. For example, sputtering of gelatin using an ion dose of 7 x 10^{16} ions/cm^2 resulted in the formation of 42 µm deep craters with 20 µm tall pillars on the crater bottom, pointed at 45° towards the gas cluster source. When the pillars reached a threshold number on the crater bottom, the sputter yield of gelatin was also seen to change, eventually stopping the sputtering. In addition, by using 40 µm polystyrene spheres embedded in gelatin, it was possible to measure the depth resolution at the film-sphere interface as a function of sputtered depth and observe when possible distortions in the 3D image occurred due to changes in the sputter rate. To minimize this distortion, a step-wise, staggered sample rotation was employed. This minimized the formation of micro-pillars on the crater bottom by changing the direction of the beam, allowing the pillars to be sputtered away and minimizing their growth. In this way, it was possible to minimize distortions in the 3D image of the embedded spheres. The depth resolutions were seen to improve from (9.4 ± 3.2) µm to (7.1 ± 1.6) µm. Using these numbers, it was possible to quantitatively measure the effect of micron-scale topography and sample rotation on the quality of the depth profile.

AS-Contributed On Demand-28 Effects of Li Deintercalation in the Electronic Structure of Li_XCoO_2 Epitaxial Thin Films*, Elena Salagre,* Dto. Fisica Materia Condensada, Univ Autonoma de Madrid, Spain*; P. Segovia,* Univ Autonoma de Madrid, IFIMAC, Spain*; M. González-Barrio,* Univ. Complutense de Madrid, Spain*; J. Pearson,* University of Maryland*; I. Takeuchi,* University of Maryland*; E. Fuller, A. Talin,* Sandia National Laboratories*; M. Jugovac, P. Moras,* Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy*; A. Mascaraque,* Dto. Física de Materiales, Fac. Ciencias Físicas, Univ. Complutense de Madrid, Spain*; E. Garcia-Michel,* Univ. Autonoma de Madrid, IFIMAC , Spain

$LiCoO_2$ (LCO) is one of the most common cathode material in rechargeable Li-ion batteries, mainly due to its high-energy capacity and good cyclability [1]. This material undergoes a complex, and not yet fully understood, set of phase transitions during Li deintercalation that plays a key role on battery performance and degradation. Stoichiometric LCO (x=1) is an insulator, but upon Li removal of 0.5% (x=0.95) it undergoes an insulator to metal transition of yet unclear origin and interpretation (Mott vs. Anderson type)[2,3]. The metallic phase has the same crystalline structure (R-3m) as the insulating one, however it has slightly different lattice parameters. These two hexagonal phases coexist in the range 0.95<x<0.75 [4]. The formation of the metallic phase is explained by hole doping of the Co t_{2g} band [5] after Li deintercalation, but the modifications experienced by the electronic structure are still controversial [2,3].

In this work we analyze high-quality epitaxial thin films of LCO grown by pulsed laser deposition on Nb-doped $SrTiO_3$(111). We perform high resolution ARPES, XPS and XAS, using synchrotron light, to characterize the electronic properties of LCO for different Li molar fraction values (x). The changes in the electronic structure during the metal-insulator transition are observed under ultra high vacuum conditions and the quality of the surface has been verified thoroughly throughout the process. We obtain detailed Fermi surfaces and constant energy surfaces, as well as band dispersion maps for the discharged (x=1) and partially charged (x<1) LCO epitaxial films. Information about the chemical and structural changes is obtained from high-resolution Co 3p, Li 1s and O 1s core levels and from the Co L and O K absorption edges.

The expected formation of Co^{4+} and of oxygen holes related to the metallization, are studied in the context of the partial hybridization of Co 3d and O 2p orbitals. We report the formation of a hole-like metallic band and measure the effective mass of the carriers, before and after Li deintercalation. A change in the band dispersion and a reorganization of spectral weights at the Fermi surface is also described for large hole doping levels. We present results that clarify the controversial topics regarding the metallization and charge compensation during Li deintercalation[4].

[1]N. Nitta et al. *Mater. Today* **2015**, *18*, 252.

[2]C. A. Marianetti at al, *Nat. Mater.* **2004**, *3*, 627.

[3]A. Milewska et al, *Solid State Ionics*, Elsevier, **2014**, 110–118.

[4]K. Miyoshi et al, *Phys. Rev. B* **2018**, *98*, 195106.

[5]T. Mizokawa et al, *Phys. Rev. Lett.***2013**, *111*, 056404.

AS-Contributed On Demand-31 Understanding the Effect of Surface Treatment on the Boehmite Scale Formation on Aluminum 6061*, Lyndi Strange,* *X. Yu, V. Shutthanandan, J. Gao, J. Son, Y. Zhang, R. Prabhakaran, K. Brooks, V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10 wt% molybdenum (U-10Mo) has been identified as a promising alternative to high-enriched uranium (HEU) for the United States High Performance Research Reactors. The nominal configuration of the U-10Mo plate-type fuel is a metallic U-10Mo fuel foil with a very thin Zr diffusion interlayer barrier clad with aluminum alloy 6061 (Al 6061). The surface of the aluminum cladding is coated with a boehmite layer to prevent corrosion in the reactor. In this work, we studied the effect of different surface cleaning treatments on the boehmite scale formation on Al 6061 using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS). ToF-SIMS provides label free and matrix free surface analysis and imaging. A complementary technique is XPS due to its surface sensitivity and ability to determine chemical and oxidation states present. In this talk, we present spectral and imaging analysis of the nanometer scale boehmite layer formed on aluminum alloy surfaces as a function of surface cleaning technique. ToF-SIMS spectral analysis shows boehmite formation on all the samples and these results are corroborated with those of XPS. ToF-SIMS spectral principal component analysis (PCA) shows a trend of surface oxidation under different pH. The boehmite interface was also analyzed using high spatial resolution ToF-SIMS imaging and XPS depth profiling. The combined ToF-SIMS and XPS approach would enhance our understanding of the nucleation of boehmite phase on these varied aluminum surfaces.

AS-Contributed On Demand-34 Using Polyamide Films Grown by Molecular Layer Deposition (MLD) on Si(111) to Form 3C-SiC Thin Film*, Rustam Amashaev,* Dagestan State University, Russian Federation*; I. Abdulagatov,* Dagestan State Uiversity, Russian Federation

Silicon carbide (SiC) is a well-known technologically important material that has many industrial applications. Thin films of SiC can be deposited by chemical vapor deposition (CVD), physical vapor deposition (PVD), or atomic layer deposition (ALD) methods, however, these techniques cannot fulfill all the industrial needs in terms of thickness control, conformality, and cost effectiveness. In this work, we explored an alternative two-step method to obtain SiC films on Si (Fig.1 in Supplemental) [1]. In the first step, MLD polyamide film deposited on silicon substrate. In the second step, the polyamide film on Si annealed at high temperatures and vacuum. Under vacuum, the hydrogen is removed from the organic film and the remaining carbon becomes a precursor in solid-state reaction with Si substrate. In contrast to other gas phase deposition techniques, MLD allows to deposit organic thin films thermally (without using plasma) with an atomic level precision and conformality. These special features of MLD enable to synthesize highly conformal and uniform SiC films. In order to demonstrate that, MLD polyamide film was deposited on Si(111) using trimesoyl chloride (TMC) and 1,2-ethylenediamine (EDA) chemistry at 120 ^{o}C [2]. Polyamide film growth rate on Si(111) was ~18.5 Å/cycle. Vacuum annealing of 1125 Å thick polyamide film for one hour at 1300 ^{o}C and 10^{-7} Torr pressure resulted in formation of ~221 Å thick crystalline film (Fig. 2a) in Supplemental). X-ray diffraction (XRD), Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS) employed to analyze annealed samples, also confirmed the formation of single crystal 3C-SiC (b-SiC) film on Si(111). Suspended ~200 Å thick 3C-SiC membrane can be formed by Si sublimation (Fig.2b) in Supplemental). Thin SiC film membranes and cantilever beams can be used in applications, such as pressure sensors, electromechanical resonators, accelerometers, and gyroscopes [3]. In general, above described approach can be applied for controlled synthesis of other metal carbide thin films as well.

[1] Amashaev R.R., et al.. Patent no. RU2020133824.

[2] Amashaev R.R., et al.. Russ. J. Phys. Chem. A., 2021, vol. 95, no. 7, p. 1440–1449.

[3] Wijesundara, M.B.J.; Azevedo, R.G. SiC MEMS devices. In Silicon Carbide Microsystems for Harsh Environments; Springer: New York, NY, USA, 2011; Volume 22, pp. 125–165.

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AS-Contributed On Demand-37 GaAs/Si Surface Energy Engineering, Modeling, and Nano-Bonding™ for Solar Cells at Low Temperatures ≤ 220°C, *A. Gurijala, P. Penmatcha, S. Jandhyala, M. Sahal, W. Peng, T. Balasooriya, T. Diaz, M. Bertram, C. Cornejo,* Arizona State University*; K. Kavanaugh,* Simon Fraser University*; R. Culbertson,* ***Nicole Herbots****,* Arizona State University

GaAs/Si tandem solar cells absorb wavelengths between 0.4 and 2 µm, and can theoretically achieve photo-voltaic conversion efficiency (PVCE) of 44%. However, current methods integrating GaAs to Si, such as hetero-epitaxy and Direct Wafer Bonding require T>400°C, leading to defects from thermal expansion mismatch in addition to lattice mismatch, and decrease PVCE. Residual native oxides also decrease PVCE.

Nano-Bonding^{TM} (NB) is a direct wafer bonding method using Surface Energy Engineering (SEE) instead of T>400°C to create more efficient solar cells. NB includes three steps at T≤ 220°C: SEE, nano-contacting, and bonding activation. SEE modifies hydro-affinity, measured via water contact angle Θ_{H2O} and surface energies, measured via g, by using wet chemical etching. SEE planarizes surfaces, terminates them via hydroxylated monolayers, and optimizes surface termination to yield 2-D Precursor

Phases (2D-PP). 2DPP are metastable and planar at the nano- and micro-scales.

3 Liquid Contact Angle Analysis (3LCAA) measures Θ_{H2O} and γ, Ion Beam Analysis (IBA) measures absolute oxygen coverage, and X-Ray Photoelectron Spectroscopy (XPS) measures surface oxidation states. 3LCAA uses statistical analysis of contact angles from 3 liquids, water, glycerin, and 1-bromo-naphthalene across wafer diameters and the van Oss-Chaudhury-Good theory. High resolution IBA combines Nuclear Resonance with <111> channeling. XPS measures Ga and As oxidation states within 5 nm of the surface.

3LCAA detects reversal in hydro-affinity of GaAs and Si after SEE. Initially hydrophobic n^{+}GaAs(100) becomes hydrophilic after SEE. γ_{GaAs} increases by almost 50% from 33.4±1 mJ/m^2 to 60±2 mJ/m^2 after SEE. Initially hydrophilic p^{+}Si(100) becomes hydrophobic with a decrease in γ_{Si} by 24% from 60±2 mJ/m^2 to 48±3 mJ/m^2. IBA detects a decrease in oxygen on GaAs of 50% from 7.2±0.5 ML to 3.6±0.2 ML after SEE. XPS reveals that two times more Ga (40%) than As (20%) is oxidized. After SEE, As_2O_5 decreases by 13.5%, while As_2O_3 increases by the same amount. IBA and XPS correlate with 3LCAA. A 50% decrease in oxygen and increase in low oxidation states lead to higher density of dangling bonds, thus higher γ and hydrophilic surface.

After NB, Surface Acoustic Wave Microscopy reveals that 98±1% of GaAs successfully nano-bonds to Si at T≤220°C with compression and 48±1% bonds without compression. A model of the GaAs surface before and after SEE is proposed to explain the reactivity and low temperature Nano Bonding of GaAs to Si.

AS-Contributed On Demand-40 Surface Characterisation of sp^2 Carbon Materials – From Graphene to Nuclear Graphite*,* ***Sarah Coultas****, J. Counsell, N. Gerrard,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc*; C. Blomfield,* Kratos Analytical Limited, UK

Carbon, considered to have ~500 allotropes varying from zero- (0D) to three-dimensional (3D) structures, is the fundamental building block of biological macromolecules. In this role it exists primarily in the sp^3 form. In more recent decades material discovery has concentrated on sp^2structures - C_{60}, carbon nanotubes (CNTs), fullerenes, graphene, graphite. Here we will explore surface characterisation techniques analysing, characterising and understanding these new material classes.

We will examine several different graphite grades using X-ray photoelectron spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS) to characterise the surface and sub-surface, particularly with regards to the sp^2 and sp^3 carbon bonding content. A peak-fitting methodology will be illustrated. Etching modes for cleaning and depth-profiling will be shown using both monatomic Ar^{+} ions and cluster Ar_n^{+} ions - the former causing unwanted damage to the graphite structure with a dramatic increase in sp^3 content. Ion implantation will be discussed for medium and high energy ions which leads to a broadening of the C 1s line. The experimental protocols will also be extended to graphene, the 2D analogue of graphite.

AS-Contributed On Demand-43 Understanding the Intrinsic Stability of Solvated Electroactive Ions at Heterogenous Mg Interfaces*,* ***Venkateshkumar Prabhakaran****, G. Johnson,* Pacific Northwest National Laboratory*; G. Agarwal, J. Howard, L. Curtis,* Argonne National Laboratory, USA*; L. Soule, S. Wi, K. Hankins, S. Thevuthasan, V. Shutthanandan, Y. Shao, R. Assary, K. Mueller, V. Murugesan,* Pacific Northwest National Laboratory

Chemical transformations of electrolyte constituents, such as solvent and solvated electroactive ions, at the Mg-metal electrode determine the evolution of the solid-electrolyte interphase (SEI) and define the performance of Mg batteries. The ability to determine the fundamental chemistry occurring at electrode-electrolyte interfaces (EEIs) during charge transfer processes as a function of both electric field strength and concentration gradient is necessary to enable the rational design of more efficient and robust electrochemical technologies for energy storage. The scientific challenge is to delineate convoluted interfacial interactions (*i.e.,* adsorption, coordination, reactivity and transport) and control reaction pathways that lead to formation of desired products over unwanted byproducts that can result in decreasing battery performance. Soft landing of mass-selected ions, a versatile approach to surface modification, is ideally suited to preparation of well-defined interfaces with predetermined electrochemically active ions. Herein, we achieved a substantial advancement in the understanding of such complex interfacial reactions on Mg battery electrodes employing precisely-defined layer-by-layer assembly of electrochemically active cations and solvated counter-ions with precisely-selected stoichiometry and concentration. As an example, ion soft landing combined with *operando* infrared reflection-absorption spectroscopy (IRRAS), Raman spectroscopy, and *in-situ* x-ray photoelectron spectroscopy (XPS) was used to characterize the decomposition of electrolyte anions and solvent molecules on Mg electrodes. Our *in-situ* multimodal analysis enabled the capture of spectroscopic signatures from key chemical transformations of electrolyte anions and solvent molecules on reactive metal surfaces. These experimental results were correlated with the evolution of the SEI layer predicted by theory to provide molecular-level insight into the reaction mechanisms. In summary, our joint experimental and theoretical approach allowed us to acquire a more delineated understanding of electrochemical transformations occurring across length scales in operating EEIs and will aid the rational design of improved and sustainable electrochemical energy technologies.

AS-Contributed On Demand-46 A New SIMS Method to Characterize Hydrogen in Polysilicon Films*,* ***Xuefeng Lin****, A. Fucsko, K. Noehring, J. Brown, E. Gabriel, A. Regner, S. York, D. Palsulich,* Corporate Laboratory, Technology Department, Micron Technology. Inc.

Abstract: A new analysis protocol for profiling the hydrogen (H) concentration depth distributions in polysilicon (poly Si) thin films on Si oxide was developed by using secondary ion mass spectrometry (SIMS). Traditional SIMS determination of H concentrations in poly Si films is to monitor and collect the atomic H^{-}, but this analysis method presents some challenges for providing stable and repeatable H depth profiles, especially for shallow profiling in thinner poly Si films on thicker Si oxide films. In this paper, we present a thorough study of the SIMS characterization of H levels in poly Si thin films on Si oxide. We describe an approach for the use of cluster SiH^- instead of atomic H^- to determine the H concentrations. The utilization of the SiH^- cluster ion minimizes both H adsorption effects on the film surface regions and also sample surface charging effects arising from the Si oxide layer underneath, thus enhancing the secondary ion signal stability in poly Si films, as discussed with secondary ion energy distribution on the samples. This method differs from conventional SIMS analysis of H in thin films and significantly improves the data quality and accuracy. We can accurately characterize H levels in 100Å-7000Å poly Si films on 1000Å-5000Å Si oxide layers. This analysis approach also shows efficiency with significant time saving to avoid often needed multiple repeat analysis in monitoring H^- atomic ion due to both H adsorption effects on the film surface regions and the e-beam induced the charge compensation effects. This analysis approach may also reduce the sample surface contamination effects in H analysis and can be applied to analyze other similar materials, such as H in Si films on other insulator films. Fourier transform infrared spectroscopy (FTIR) analysis was used to study the Si-H chemical bonding information for investigating the nature of the SIMS collected SiH^- cluster ions. Both the H implant sample with no significant Si-H bonding, and the poly Si samples with high levels of H and the weak Si-H bonding, exhibited strong SiH^- secondary cluster ion intensities in our studies. This indicates thecluster ion signals arise from either the combination of Si and H ions through the physics formation process or weak chemically bonded Si and H.

*Index Terms:*Hydrogen, FTIR, Ion Energy, Polysilicon, SIMS

AS-Contributed On Demand-49 Crystal Anisotropy in Surface Energy Engineering(See) OF $LiTaO_3$(110) Piezo-Electric for Low Temperature (< 453 K) Nano-Bonding™ to SI and A-Quartz SiO_2*, S. Prakash, M. Sahal, A. Elison,* ***Shreyash Prakash****, B. Baker, S. Narayan, L. Puglisi, R. Culbertson, N. Herbots,* Arizona State University

Voice activated chips require integration of piezoelectrics on Si to respond to sound. One group of piezoelectrics, Lithium-based metallic oxides ($LiXO_3$), are strong candidates for voice activated chips due to their large piezoelectric coefficient (d_{33}). $LiTaO_3$ has a d_{33} of 5.7 pC/N and $LiNbO_3$ has a d_{33} of 6.0 pC/N, whereas SiO_2 has a d_{33} of only 0.14-0.26 pC/N. This work investigates bonding piezoelectric $LiTaO_3$ to Si.

Monolithic integration of dissimilar materials combines each material into a continuous heterostructure. Current wafer integration methods include heteroepitaxy, which is ordered crystal growth on another crystal surface, and Direct Wafer Bonding (DWB), which bonds crystal wafers via high-temperature annealing. But $LiTaO_3$ has a highly anisotropic trigonal crystal structure, while Si, with its cubic diamond structure, is much more isotropic. Si cubic lattice spacing happens to be much smaller than $LiTaO_3$'s. This means that $LiTaO_3$ crystals are heavily mismatched to Si crystals in all three directions, by as much as 40% in the c-direction and 66% in the a-direction.

Hence, trying to bond $LiTaO_3$ to Si via heteroepitaxy would lead to very large mechanical strains and significant crystal defects at the bonding interface. In addition, the large lattice mismatch could also generate fractures in brittle $LiTaO_3$. Both heteroepitaxy and DWB also use temperatures above 400°C for wafer annealing. $LiTaO_3$ and Si have a very large coefficient of thermal expansion (CTE) mismatch: $LiTaO_3$ has a CTE of 18.3 x 10-6/K, which is roughly 8 times greater than Si's CTE of 2.3 x 10^{-6}/K, and about 25 times greater SiO_2's CTE of 0.75 x 10^{-6}/K. Moreover, $LiTaO_3$ decomposes into Ta_2O_5 and Li^+ at T > 400°C. Hence, neither heteroepitaxy nor DWB are suitable integration methods for bonding $LiTaO_3$ to Si. Therefore, this investigates Nano-Bonding^{TM,1} (NB) of $LiTaO_3$ to Si at room temperature.

NB uses Surface Energy Engineering (SEE) to modify the surface energies(γ^T) of crystal wafers into far-from-equilibrium states. SEE creates complementary, far-from-equilibrium two-dimensional precursor phases to catalyze bonding. SEE uses Three Liquid Contact Angle Analysis (3LCAA) and the van Oss-Chaudhury-Good theory to characterize and measure hydro-affinity (HA) and γ^T, which indicate the degree of interaction between the two surfaces. 3LCAA can map γ^T along different crystal orientations. Water contact angles on anisotropic $LiTaO_3$ are found to vary significantly by 40%, averaging 45 ± 5.4°, with a range of 17 ± 1°, larger than $3\sigma = 3 \times 5.4° = 16.2°$. The observed effect of anisotropy upon surface HA is then correlated with γ^T, which fluctuates ± 6% with crystal directions. The effect of crystal anisotropy on the NB of $LiTaO_3$ to Si will be discussed based on HA and γ^T variation.

AS-Contributed On Demand-52 Coincident XPS and Raman Analysis of Drug Composition Phases in a Pain-Killing Tablet*,* ***Paul Mack,*** Thermo Fisher Scientific, UK

The benefits of configuring a single surface analysis tool with both XPS and Raman spectroscopy has previously been demonstrated for materials such as TiO_2, MoS_2 and graphene.This multi-technique analytical method is particularly useful in the context of ion sputtering, such as using argon clusters to clean the PMMA residue from a graphene surface, where XPS can be used to monitor chemical/compositional changes and Raman can be used to detect whether the ion sputtering is damaging the graphene lattice.Another important use for the combined XPS/Raman approach is where the sample is optically homogeneous or sample features are optically invisible.Either XPS or Raman could be used to find the features/areas of interest, but once found, if the analyst has to move the sample to a completely separate tool for further analysis, then it will be very difficult to locate exactly the same analysis feature/area.

Coincident XPS/Raman, with both techniques set-up to look at the same spot on the same sample, is the ideal technique to analyse optically invisible or homogeneous samples.In this work, a pain-killing tablet was analysed to detect to the various drug components, using Raman to specifically identify the drug and XPS to quantify the elemental/chemical states and evaluate the functional groups in the organic compounds.XPS was also used to image the surface, with full C1s, N1s and O1s spectra collected at each imaging pixel.It was then possible to use processing techniques, such as Principal Components Analysis (PCA) or Non-Linear Least Squares Fitting (NLLSF) to generate chemically resolved maps of the tablet.

AS-Contributed On Demand-55 Advancing Multimodal Imaging of the Evolving Interface of Irradiated Materials*,* ***Xiao-Ying Yu****, J. Yao, S. Spurgeon, B. Matthews, S. Riechers, Z. Zhu, W. Luscher,* Pacific Northwest National Laboratory

Multimodal imaging has seen renewed interest in microanalysis and microscopy. Light microscopy and electron microscopy are the two main pillars in correlative imaging in microanalysis. More advanced chemical imaging tools, especially time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a powerful imaging mass spectrometry technique, has got introduced into the repertoire of imaging and spectroscopy modalities in recent years. Sample preparation is an important aspect in enabling multimodal imaging of the same sample. The sequence of sample analysis is another crucial factor to consider in achieving successful results. In this talk, I will present recent multimodal imaging results of irradiated cladding samples from a commercial heavy water reactor to probe the evolving material interfaces. Because the cladding materials have been exposed to neutron irradiation, sample handling is demanding. We used SEM-FIB to lift out a small section of the sample from the cladding material to permit atomic force microscopy (AFM), ToF-SIMS, and transmission electron microscopy (TEM) multimodal imaging of irradiated cladding. When comparing irradiated vs. un-irradiated samples, 3D distributions of isotopic hydrogen and lithium of the cladding indicate unexpected material transport as a result of neutron irradiation. This novel analysis sequence of irradiated commercial water reactor cladding material demonstrates that the advancement of correlative imaging can bring more scientific understanding of the water reactor technology and improve technical applications in the future.

AS-Contributed On Demand-58 Quantum Considerations About the Magic Angle in XPS Equipment*,* ***Alberto Herrera-Gomez,*** Cinvestav-Unidad Queretaro, Mexico

Bragg diffraction is employed as a means for monochromatizing X-rays in various spectroscopies such as X-ray photoelectron spectroscopy (XPS), X-ray absorption, X-ray diffraction, etc. The Bragg reflection causes a partial polarization of the beam impinging the sample. In fact, Bragg-reflection is commonly employed as a means for polarizing X-ray beams [1]. It was not until year 2010 that the partial polarization caused by the monochromator in XPS instruments was reported as a required correction for the calculations of the electron core-level photoelectric cross section [2]; the associated correction could be up to 10%.

The partial polarization also affects the so-called “magic angle”, which refers to the angle at which the photoelectric cross section does not depends on the core-level asymmetry factor. The quantification of the change on the magic angle is reported in Ref. [3]. The correction on the photoelectric cross-section was done by averaging over initial polarizations [2]. This is the rule employed when calculating cross-sections in optical and electron physics [4–6]. An issue that is not discussed in the textbooks is that this assumption implies that Bragg-reflected photons imping the sample as either σ-polarized or π-polarized with probabilities depending on the polarization direction of the photon before reflection (this is referred as the hypothesis of the collapse of the X-ray photon wave-function upon Bragg diffraction) [3]. The other possibility is that the reflected photons are elliptically polarized. This is assumed in important works such as that described by Hart in 1978 [7]. In the first case, the magic angle (58.7°) differs by 4° from the value usually employed (54.7°). In the second case, the magic angle only changes by 2°. The experiments required to distinguish between the two cases will be discussed.

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AS-Contributed On Demand-61 Optimization and Characterization of Isotopically-Labeled, Epitaxial Fe_2O_3 and Cr_2O_3 for Diffusion Studies*, **Tiffany Kaspar**, S. Taylor, K. Yano,* Pacific Northwest National Laboratory*; T. Lach,* Oak Ridge National Laboratory*; Y. Zhou,* Pacific Northwest National Laboratory, USA*; Z. Zhu,* Pacific Northwest National Laboratory*; A. Kohnert,* Los Alamos National Laboratory*; E. Still, P. Hosemann,* University of California at Berkeley*; D. Schreiber,* Pacific Northwest National Laboratory

In virtually every area of materials science, it is critical to understand the movement of atoms within solids under external stimuli such as temperature, pressure, electric fields, magnetic fields, irradiation, chemical gradients, and/or concentration gradients. This movement often takes the form of diffusion. In oxides, anion and cation diffusion can be significantly different, and both can be dependent on factors such as oxide stoichiometry and/or oxygen activity in equilibrium with the oxide, which greatly increases the complexity of observed phenomena. This diffusion is exploited for energy generation and storage in, for example, batteries and solid oxide fuel cells, and electronic devices such as resistive switching memory. Irradiation by energetic particles alters both the magnitude and the mechanism(s) of diffusion in solids by introducing a non-equilibrium population of vacancies and self-atom interstitials as a result of atomic displacements. This high concentration of defects serves to enhance diffusion, significantly impacting microstructural evolution in radiation environments. Here, we present a universal approach to the deposition of epitaxial oxide thin films in which anions, cations, or both can be isotopically enriched at specific locations within the film stack. We demonstrate this approach using epitaxial thin films of Fe_2O_3 and Cr_2O_3 in which precisely-defined layers isotopically enriched in ^{18}O and/or ^{57}Fe have been included. Complementary characterization by scanning transmission electron microscopy (STEM), atomic probe tomography (APT), and secondary ion mass spectrometry (SIMS) establishes the position, concentration, and interfacial abruptness of the isotopically-enriched layers. We demonstrate the utility of this approach by quantifying oxygen and cation self-diffusion in pristine epitaxial Fe_2O_3 and Cr_2O_3, as well as at structural defects in mixed-phase epitaxial Fe_2O_3/Fe_3O_4. Diffusion induced by thermal annealing is compared to that enhanced by proton irradiation by quantifying the distribution of an ^{18}O (and in some cases, ^{57}Fe) layer intentionally placed within the oxide thin film.

AS-Contributed On Demand-64 Adsorption Study of L-Cysteine Self-Assembled Monolayers on Au (100) Surface by Scanning Tunnelling Microscopy and Ab-Initio Methods*, V. Franco, S. Rodríguez-Sotelo ,* Instituto de Física del Litoral (CONICET-UNL), Argentina*; G. Ruano-Sandoval,* Centro Atómico Bariloche (CNEA), Argentina*; M. Passeggi (h),* Instituto de Física del Litoral (CONICET-UNL) , Argentina*; **Florencia Calaza**,* Instituto de Desarrollo Tecnológico para la Industria Química (CONICET-UNL), Argentina

The functionalization of metal surfaces by biological molecules has a growing number of applications in various fields. For this, it is essential to understand the chemical and physical properties of the organic /inorganic interface and the formation process of self-assembled monolayers (SAM's) of biological molecules such as amino acids. L-cysteine (Cys) is a particularly interesting amino acid as a macromolecule binder and chemical sensor. In this work, we carry out a theoretical and experimental study of the formation of SAM's of Cys molecules on monocrystalline surfaces of Au (100), in order to clarify the molecular adsorption mechanism. The adsorption of molecules was performed by dipping the substrate in methanolic solutions of Cys at different coatings and characterized by scanning tunneling microscopy (STM) in air and at room temperature. Additionally, the substrate-adsorbate interaction was studied with ab-initio calculations using the Density Functional Theory (DFT) in three systems: (i) Cys on Au (100), (ii) Cys trimers on Au (100) and (iii) Methanol on Au (100), to determine the equilibrium configurations, adsorption energies and distances, state densities and charge transfer between the substrate and the molecule.

By scanning tunnel microscopy, the molecular structure, order and reconstruction that induce the chemisorption and /or physisorption process of these molecules in the substrate were examined. It is revealed a pattern in the form of rectangular bands of Cys molecules, adsorbed as multilayers on Au (100). The calculations showed that the physisorption processes of Cys on Au (100) are mainly directed by the interaction between the thiol group and gold. The most stable configuration and the difference in charge density induced by the interaction, for this system, indicate that the amino acid is in its zwitterionic form. Furthermore, it was determined that the amino functional group moves away from the gold surface with a positive charge density, exposing the carboxyl group with a negative charge density closer to the surface; which would explain the chemical composition of SAM's. The latter possibility was tested by ATR-IR (Attenuated Total Reflectance-IR) to try identifying which groups of the molecule are interacting more strongly with the surface Au atoms.

AS-Contributed On Demand-67 Navigating Disorder in Superconductors Using Atomic-Scale Imaging and Machine Learning*, **Petro Maksymovych**,* Oak Ridge National Laboratory

Disorder is a powerful approach to elicit and control superconducting properties, as evidenced from record Tc's, quantum phase transitions and exotic quasiparticles, predicted or evidenced from disorder interacting with the superconducting order parameter. Capturing and understanding effects of disorder necessitates bridging length, energy and temporal scales - a persistent challenge for experiment and theory. Here we will categorize disorder in notoriously heterogeneous atomic-scale images of unconventional superconductors. From the information centric point of view, understanding the structure of these datasets amounts to effective and physically meaningful data compression. We will discuss compressibility of various kinds of STM data setting up the context for techniques of compressive sensing, machine learning and information theory as a way to understand the results of the experiments and improve data acquisition. We will promote similarity learning as a consistent strategy to categorize disorder with minimum prior knowledge. And finally, we will show how disorder helps understanding the STM technique itself, using statistical identification of Josephson currents in tunneling microscopy. Research sponsored by Materials Science and Engineering Division, US DOE and Center for Nanophase Materials Sciences, Oak Ridge National Lab, a DOE Office of Science user facility.

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AS-Contributed On Demand-70 Overview of *JVST A* Collection of Guides and Best Practices for XPS*, Don Baer,* Pacific Northwest National Laboratory*; K. Artyushkova,* Physical Electronics USA*; C. Easton,* CSIRO Manufacturing, Australia*; M. Engelhard,* Pacific Northwest National Laboratory*; G. McGuire,* Adámas Nanotechnologies, Inc.,*; A. Shard,* National Physical Laboratory, U.K.

The rapid growth in the use of XPS around the world has introduced the technique to a wide range of researchers in many disciplines with important areas of application. Unfortunately, the experience and practices well established in the XPS community have not as readily transferred to this growing group of new users. This has led to a significant number of inaccurate, misleading or fundamentally incorrect applications of XPS or analysis of XPS data as reported in the literature. In response to the issue, and the more general reproducibility challenges, the Journal of Vacuum Science and Technology A has published a collection of papers under the heading *Reproducibility Challenges and Solutions with a focus on XPS*. Because of the wide use of XPS, a series of XPS guides and protocols were included in this collection. This talk provides an overview of the information provided by the papers. The approach taken to assembling the guides was to break the overall topic into guides that address specific areas or issues. Some papers are relevant to most types of XPS studies while others focus on applications of XPS to specific areas or topics. General XPS topics covered in one or more papers include an introduction to XPS and issues related to quantification, backgrounds in XPS spectra, peak fitting, electron path lengths important to analysis, dealing with insulators and surface charging, the importance of consistent terminology, instrumentation performance checks, information about relevant international standards, and data conversion and storage. These guides are intended to be more introductory than comprehensive although they point readers towards relevant literature that covers some topics in greater depth. The application area guides are intended to provide specific information related to the use of XPS in important areas. These guides address XPS analysis of polymers, catalysts, semiconductors and nanoparticles. This collection of papers has been developed in response to a survey and discussions that identified needs for tools that can help the community address reproducibility issues. In addition to presenting a summary of this collection, we request feedback from the community and suggestions for other tools that can assist the AVS in addressing consistency and reproducibility challenges, especially in areas of importance to surface analysis. A list of papers in the collection can be found at: https://avs.scitation.org/toc/jva/collection/10.1116/jva.2020.REPROD2020.issue-1.

AS-Contributed On Demand-73 Surface Functionalization and Atomic Layer Deposition of Binary Metal Oxides on Mos$_2$ Surfaces*, Theodosia Gougousi,* *J. Kropp, C. Ataca,* UMBC

Transition metal dichalcogenides (TMD) have been studied for device applications due to their electronic properties and their possession of a bandgap (1.8eV for single layer MoS_2).The fabrication of electronic devices requires deposition of high-quality dielectrics on the hydrophobic TMD surface and remains a challenge.

In this work we will provide examples of TiO_2 and Al_2O_3 Atomic Layer Deposition (ALD) film growth from tetrakis dimethyl amino titanium (TMDAT), trimethyl aluminum (TMA) and H_2O at 100-200°C on exfoliated and Chemical Vapor Deposition (CVD) MoS_2 flakes. We find that the initial surface condition of exfoliated MoS_2 flakes varies greatly due to residual adhesive contamination resulting in large variation in the film morphology. More controlled growth is obtained for CVD MoS_2 flakes but even in this case the surface coverage is thickness dependent for films as thick as 10 nm.

In order to alter the surface energy, seeding with inorganic and organic species have been investigated. Mercaptoethanol (ME) is a small thiol that contains a -SH functional group at one end and -OH termination at the other end. The -SH termination is expected to react with the MoS_2 surface leaving the surface -OH terminated as desired for the onset of the ALD chemistry. Atomic Force Microscopy (AFM) measurements confirm that ME treatment alone does not promote more uniform film growth. Computational studies of the ME-MoS_2 surface interaction using Density Functional Theory (DFT) reveal that ME interacts with the sulfur vacancies almost exclusively. Vacancy density is less than ~5% for as-deposited CVD MoS_2, and depositions result in non-continuous coverage for typical thermal ALD.Argon ion sputtering was used to remove Sulfur atoms from the surface and increase the vacancy density up to ~20%. AFM confirms the formation of continuous 6 nm TiO_2 films at 100°C for both ME treated and control samples.DFT calculations reveal that TDMAT can interact directly with the vacancy. However, the calculated Density of States for these defect rich surfaces contain gap states that are undesirable for high quality devices. Treatment of defect rich surfaces with ME results in the removal of the gap states which is expected to result in good electrical properties.

$HAuCl_4$ solutions have been also used to seed the surface with -Cl terminal species to initiate film growth. XPS data confirm both the presence of Au on the surface and absence of residual chlorine. AFM shows only partial surface coverage for films as thick as 6 nm. A distinct difference in the film morphology is obtained though as a result of this treatment indicating that the film growth mechanism has been altered.

AS-Contributed On Demand-76 Elucidating the Lubrication Mechanism of Ionic Liquid: a Multi-technique, Nanoscale Spectroscopy and Microscopy Study*, Filippo Mangolini,* *Z. Li, O. Morales-Collazo,* The University of Texas at Austin*; J. Sadowski,* Brookhaven National Laboratory*; H. Celio, A. Dolocan, J. Brennecke,* The University of Texas at Austin

Ionic liquids (ILs) have recently gained considerable attention owing to their unique and tunable physico-chemical properties (*e.g.*, low vapor pressure, high thermal stability), which have made them useful for a range of applications, including energy storage, catalysis, and lubrication. ILs are particularly attractive in lubrication, since their properties make them suitable for components working under extreme conditions, such as those found in engines and spacecraft. When ILs are used as lubricants, the interface between the IL and the sliding surfaces plays a pivotal role in controlling the friction and wear response. Despite the weight of published literature, remarkably little is still known about the lubrication mechanism of ILs. The development of a fundamental understanding of the mechanism by which ILs reduce friction and/or wear requires shedding light on the processes occurring at nanoscale asperities within macroscale contacts. This constitute a significant challenge that requires the use of complementary surface-analytical techniques to understand the nanoscale mechanisms at play.

Here, we used atomic force microscopy (AFM) to visualize and quantify the processes occurring at sliding interfaces *in situ*, in single-asperity nanocontacts. The AFM tests, in which a diamond tip was slid on iron in phosphonium phosphate IL (PP-IL), indicated a significant friction reduction only after the removal of the native surface oxide from iron. Even though the AFM experiments allowed for the identification of changes in topography and friction, they could not provide any information about the composition of the regions scanned by AFM. The analysis of these regions is a challenging surface science problem owing to their limited dimensions and the small thickness of the surface material modified by the mechanical action of AFM tips. To address this challenge and elucidate the origin of the friction reduction observed by AFM, a multi-technique approach was employed. The results of laterally-resolved *ex situ* analyses of the surface chemistry of steel by synchrotron-based X-ray photoemission electron microscopy, low energy electron microscopy, and time-of-flight secondary ion mass spectrometry indicated that the mechanically-induced exposure of metallic iron during AFM tests carried out in PP-IL leads to an increase in surface coverage of adsorbed phosphate anions together with a change in surface potential. Based on these results and atomistic simulations of the configuration geometry of phosphate ions on metallic and oxidized iron, a simple phenomenological model is proposed to account for the observed lubrication behavior.

AS-Contributed On Demand-79 Hydrogen Detection by SnO_2-Based Core-Shell Nanowires With Varying Shell Thicknesses Grown by Atomic Layer Deposition*, Muhammad Hamid Raza,* Humboldt-Universität zu Berlin, Germany*; N. Kaur, E. Comini,* University of Brescia, Italy*; N. Pinna,* Humboldt-Universität zu Berlin, Germany

Hydrogen is one of the most potent energy vectors due to its low weight, high catalytic values, non-pollution, and high abundance. There is a need for quick and sensitive hydrogen detection, due to its nature as a colorless and odorless extremely flammable gas with a low explosive limit (4%, 40000 ppm) in air. SnO_2 nanostructures have been extensively reported semiconducting metal oxide (SMOX) for gas sensing. The sensitivity and selectivity of these nanostructured can be enhanced by employing them with the secondary materials.However, control over the thickness of the shell layer is essential; in particular, a thin shell layer may influence the charge conduction channel by modulating the space charge layer near the interface. Here, two different SnO_2-based core-shell nanowires (CSNWs) are synthesized with the loading of *p*-type SMOX (NiO) and insulating (SiO_2) films as secondary materials onto the SnO_2 nanowires. Atomic layer deposition (ALD) was used to deposit varying thicknesses of NiO and SiO_2

shell layers. Interestingly, both the heterostructures are found to exhibit enhanced sensitivity to hydrogen in spite of underlying different sensing mechanisms. Importantly, the thickness of the shell layer plays a significant role in both types of heterostructures., *i.e*., SnO_2-NiO and SnO_2-SiO_2 CSNWs. A comparison of enhanced selectivity and sensitivity after the ALD grown shell-layers will be presented in terms of *p–n* heterojunction (SnO_2-NiO CSNWs) vs. molecular sieve action (SnO_2-SiO_2 CSNWs).

AS-Contributed On Demand-82 X-Ray Absorption Near Edge Structure (XANES) Measurements of Oxides Formed on High Entropy Alloys*, **Anil Krishna Battu**, B. Gwalani, T. Suntharampillai, A. Devaraj,* Pacific Northwest National Laboratory

High entropy alloys (HEA) exhibit an excellent combination of properties, providing motivation to novel alloy development with single or multiphase microstructures. High temperature application of HEAs requires comprehensive understanding of phases tability and environmental degradation. The equiatomic CrMnFeCoNi based alloy, also known as Cantor alloy, is a widely studied single-phase alloy for its superior structural properties. However, recent studies have demonstrated the formation of secondary phase during the annealing in the intermediate temperature ranges. We investigated the structural and chemical changes in Cantor alloy during elevated temperature oxidation using in situ and ex situ approaches along with the influence of Al addition to the alloy composition. We utilized Cr, Mn, Fe, Co and Ni L edge X-ray absorption near edge structure (XANES) measurements to understand the chemical changes in the material. The structural and phase changes were analyzed using transmission electron microscopy (TEM) and atom probe tomography (APT). The oxidation states of the elements can be clearly identified from the XANES spectra and correlated to the phase information obtained from TEM and APT. Addition of Al changes the oxide chemistry, material vulnerability to oxidation and these details will also be discussed.

AS-Contributed On Demand-85 Laser Desorption Postionization vs. Secondary Ion Mass Spectrometry for Imaging of Organic Biomarkers in Geological Sample*, R. Wickramasinghe, M. Pasterski,* University of Illinois at Chicago*; A. Ievlev, M. Lorenz,* Oak Ridge National Laboratory*; I. Veryovkin, F. Kenig, **Luke Hanley**,* University of Illinois at Chicago

Multidimensional gas chromatography mass spectrometry (MS) has been used to detect organic biomarkers within bulk extracts of geological samples [1]. However, it is difficult to rule out the possibility of organic contamination in such studies due to the loss of spatial information during sample preparation. MS imaging and other spatially resolved sampling methods can overcome these shortcomings by identifying organic biomarkers within intact geological samples and correlating such MS data with petrographic and fluorescence images. Secondary ion mass spectrometry (SIMS) imaging is currently the premier method for identifying organic biomarkers within geological samples [2], but suffers from extensive ion fragmentation that can limit molecular identification.

A novel MS imaging strategy is described here that seeks to improve upon SIMS imaging of organic biomarkers within geological samples. Femtosecond laser desorption postionization mass spectrometry (fs-LDPI-MS) employs 800 nm, ~75 fs laser pulses for ablation of neutral organic molecules from a thin prepared slice of a geological sample, followed by postionization using 157 nm (7.9 eV) laser pulses and subsequent detection by a time-of-flight mass analyzer [3].

The high lateral resolution of fs-LDPI-MS imaging and its ability to detect molecular species with lower fragmentation relative to SIMS allows for high resolution MS-imaging and identification of isolated sample features. Multimodal imaging of geological samples with high organic content is conducted with Bi ion ToF-SIMS, fs-LDPI-MS, petrographic, and fluorescence imaging. SIMS and fs-LDPI-MS specifically are compared for their relative ability to identify organic biomarkers confined to micron-sized regions within intact geological samples.

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AS-Contributed On Demand-88 Box Plots: A Simple Graphical Tool for Visualizing Overfitting in Peak Fitting as Demonstrated with X-ray Photoelectron Spectroscopy Data*, **Behnam Moeini**, H. Haack,* Brigham Young University*; N. Fairley,* Casa Software Ltd, UK*; V. Fernandez,* CNRS, Institut des Matériaux Jean Rouxel, IMN, Université de Nantes, France*; T. Gengenbach , C. Easton,* Commonwealth Scientific and Industrial Research Organization (CSIRO) Manufacturing, Australia*; M. R.Linford,* Brigham Young University

Peak fitting of spectra/data is frequently performed in science. However, recent reports suggest that the quality of this peak fitting in the scientific literature is often inadequate. An important step towards improving the peak fitting in the literature is to develop the expectation/culture that the testing of one's fitting protocol, along with the presentation of such tests, is necessary for confirming the validity of a fit. The development of new methodologies that enable researchers to visualize the qualities of their fits that are straightforward to implement will aid in this effort. In this paper we describe a new statistical tool for determining the quality of protocols for fitting data. This tool, box plots of the results of random starting conditions, helps identify multiple local minima in a multidimensional fit space of the fit parameters. Ideally, there should be a single global minimum for a fitting protocol such that different, reasonable starting conditions lead to the same result. To determine whether a fit space contains multiple local minima, a series of reasonable, random starting conditions are chosen for the fit. If the boxes in the box plot of the peak areas of these fits are narrow, the different possibilities converge to a single global minimum. Conversely, if the boxes are wide, multiple local minima are present. This method is similar to the mathematical concept of 'disproof by contradiction'. Our approach is demonstrated with four- and ten-component fits to a moderately complex C 1s X-ray photoelectron spectroscopy (XPS) narrow scan. The resulting box plots compare favorably to results of traditional Monte Carlo analyses and uniqueness plots, where box plots are applied to Monte Carlo results, although each of these statistical tools performs a different function/probes a fit space/protocol differently.

AS-Contributed On Demand-91 A New Compact Electron Detector for REELS and Elastic Peak Spectroscopy*, **Philippe Staib**,* Staib Instruments

Several analysis techniques are performed using a new single electron detector mounted into an SEM chamber. The primary applications are REELS and Elastic Peak Spectroscopy (EPS) at primary beam energies up to 5000 eV.The detector is an energy analyzer with multiple operating modes:

- Imaging the secondary electron SE and back scattered secondary electrons BSE signals with precise selection of the energy range.

- Imaging the Elastic peak and measurement of its intensity and energy position.

The measurement and mapping of the elastic peak fully separated from energy losses is a powerful technique for sample characterization. The peak intensity is determined by the elastic backscattering cross section and primarily depends on the atomic number Z thus sensitive to the atomic composition (identification of phases). Measurements also reveal minute changes of the crystal structure. The energy position is determined by the recoil energy loss, owing to the conservation of energy and impulse, and depends on the atomic mass M of the target atom. The energy of the elastic peak shows shifts expected from the recoil loss energy, measurable, in this case, for lower Z materials from H up to O.

- Measuring energy losses of characteristic energy losses (CEL) especially the low energy valence band region and band gap of semiconductors.

- Mapping the spatial distribution of energy losses.

- Mapping the photon emission (cathodo- luminescence, surface plasmon decay) by setting the analyzer above the primary energy in order to block the electron signal.

When operating at higher beam current intensities, Auger electron spectroscopy (AES) and measurement of the total X-ray yield are possible. Diffraction patterns are observed at higher primary beam energy when adjusted to a grazing incidence angle to the surface (EBSD or RHEED).

These operating modes are illustrated by results obtained on metals, semiconductors and biological samples, and also show the necessity of a clean, carbon free, vacuum environment to gain the most from these capabilities.

The various operating modes of the detector are selected simply by adjusting its control voltages of the and are easily computer controlled. The detector works up to 5,000 eV, a beam energy well suited to SEM columns. The electronically adjustable energy resolution can reach 1eV to provide accurate measurements of the elastic peak and energy losses. The sensitivity, resulting from the analyzer's large acceptance solid angle, allows work in the nano ampere beam current range for most applications. Combining these capabilities in a single energy detector adds new analytical tools to SEM.

AS-Contributed On Demand-94 In Situ Spectroscopy Beamline at the Swiss Light Source*, **Zbynek Novotny**,* University of of Zürich & Paul Scherrer Institute, Switzerland

A new In Situ Spectroscopy beamline (X07DB) has been recently established at the Swiss Light Source (SLS). The beamline is now open to the user community *via* proposal access, offering studies of solid-gas and solid-liquid interfaces using ambient-pressure X-ray photoelectron spectroscopy. Two experimental endstations are available, capable of studying "real" catalysts such as polycrystalline/powder samples under catalytically relevant conditions, as well as model systems represented by well-defined single crystals prepared under UHV conditions. The unique capability of the beamline is the ability to perform electrochemical studies. Besides our current experimental capabilities, I will present the ongoing in-house research, instrumental development, and plans towards the scheduled upgrade of the SLS 2.0.

AS-Contributed On Demand-97 The Frequency with which the Elements are Researched and their X-ray Photoelectron Spectroscopy (XPS) Narrow Scans are Shown in the Scientific Literature*, G. Major, G. Pinto, V. Carver,* Brigham Young University*; C. Easton, T. Gengenbach,* CSIRO Materials Science and Engineering, Australia*; W. Skinner,* Future Industries Institute, University of South Australia, Australia*; D. Baer,* Pacific Northwest National Laboratory*; T. Nunney,* Thermo Fisher Scientific, UK*; **Matthew Linford**,* Brigham Young University

A recent report written by some of us (Linford … Baer, Microscopy and Microanalysis 2020) indicates that more than 30% of the X-ray photoelectron spectroscopy (XPS) narrow scans in the scientific literature are incorrectly analyzed. In this context, we present a discussion of the frequencies with which the different elements are researched for XPS peak fitting and reported in the scientific literature. That is, we have correlated the number of page views from XPS Simplified, which is an often-accessed online database on XPS peak fitting, with the numbers of narrow scans for the different elements that are published in different materials journals. In general, there is good correlation between the elements on these lists (especially between the top ten elements on both lists, but less so among the next ten), with carbon and oxygen being the top two elements on both lists. In this analysis, it became clear that there are certain elements that are more researched on XPS Simplified and less shown in the literature, and vice versa. A possible interpretation for these results is that those elements that are more often shown in the literature and less researched are considered by the community to be more straightforward or easier to analyze, while those that are less shown and more researched are considered to be harder. We compare these perceptions of 'easier' and 'harder' to the accuracy with which these elements are analyzed in the literature. Also, in an effort to better understand the two most commonly researched and published-on elements (C and O) in XPS, we discuss the types of carbon- and oxygen-containing materials that are most often analyzed by XPS in the literature. That is, we will present the fraction of papers that show carbon analysis of polymers vs. graphitic carbon materials (graphene, carbon nanotubes, C60 fullerenes, etc.) vs. adventitious carbon, etc. For oxygen, we discuss the fraction of papers that show XPS analysis of inorganic oxides vs. polymers. Finally, using principal component analysis (PCA), we discuss the differences and similarities between the different journals and XPS Simplified vis-à-vis the different elements that are shown or researched.

AS-Contributed On Demand-100 Correlative Experimental and Theoretical Investigations of the Interfacial Bond Formation of Ti, Al, and TiAl Thin Films Deposited on Polycarbonate*, **Lena Patterer**, P. Ondracka, D. Bogdanovski, L. Jende, J. Schneider,* RWTH Aachen University, Germany

To systematically investigate the interfacial bond formation between poly(bisphenol A carbonate) (PC) and TiAl thin films, this study explores also the individual effects of Ti and Al on the bond formation at the interface. Therefore, thin metallic layers (Ti, Al and TiAl) were deposited onto PC substrates by direct current magnetron sputtering and the forming interface was subsequently analyzed by X-ray photoelectron spectroscopy (XPS). In addition to the experimental analysis, density functional theory molecular dynamics (DFT-MD) simulations of a thermalized PC dimer interacting with the corresponding metallic surfaces were carried out to study the interface regarding reactivity, bond density and bond strength. To this end, selected configurations at various simulation times were used to determine changes in the chemical state of the polymer in comparison to the experimentally detected changes. Consistent with DFT predictions, XPS data indicate a high reactivity of Ti towards PC. Reactions between Ti atoms and all functional groups of PC are observed, resulting in the formation of interfacial C-Ti as well as (C-O)-Ti bonds for Ti and TiAl thin films. In contrast, Al is less reactive and reacts only with the carbonate group to form (C-O)-Al bonds at the interface. However, integrated crystal orbital Hamilton population calculations indicate a significantly higher bond strength for interfacial (C-O)-Al bonds (up to −5.6 eV) compared to interfacial (C-O)-Ti and C-Ti bonds (both up to −2.6 eV).

In summary, the experimentally obtained density of interfacial bonds is significantly higher for the Ti thin film compared to the Al thin film, but the bond strength between Al atoms and the carbonate groups is higher. By multiplying the experimentally determined relative interfacial bond concentration with the theoretically determined bond strength as an indicator for adhesion, Ti exhibits a more than five-times higher value compared to the Al thin film. Consequently, this study is unequivocal evidence of Tithin films being the preferential choice as adhesion interlayers for PC.

AS-Contributed On Demand-103 Analysis of XPS Depth-Profile Data Using Maximum Likelihood Reconstruction: Extracting Sample Structure and Sputtering Parameters*, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both sample structure and composition and sputtering parameters from XPS depth-profiles of multilayer films. Such data are typically used to obtain the apparent fractional composition of each element as a function of depth. These results are apparent because the analysis assumes the elements are homogeneously distributed in the probed region, a condition which necessarily does not hold near interfaces. Furthermore, the sputtering process leads to roughening, in-sample mixing, and changes in sample composition, which also lead to further distortions.

Our approach to analysis of depth profiles is first to construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm.

We first demonstrate the basic idea and explore the type of results that can be obtained using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. This is especially true when peaks at very different energies are used, as they have very different inelastic mean free paths and so provide complementary information. We then reconstruct experimental data from several well-characterized samples and discuss the results obtained. Finally, the possibility of optimization against complete spectra (rather than extracted fractional compositions) and inclusion of angle-resolved data are considered.

AS-Contributed On Demand-106 Formation of Black Silicon-Like Nanostructures During Flat-Top Femtosecond Laser Ablation in Atmosphere*, **Jason Gross**, L. Hanley,* University of Illinois at Chicago

The fluence and transverse optical intensity profile of a laser beam are crucial parameters for high resolution depth profiling analysis of materials by femtosecond laser ablation (fs-LA) mass spectrometry. When a conventional Gaussian-shaped fs beam is used for ablation, material removed from the crater walls leads to artifacts in the depth profile. This same Gaussian fs beam can be conditioned into a flat-top shape with homogenized fluence and used for fs-LA in atmosphere. Ablation with the flat-top fs beam appears to prepare nearly cylindrical craters with flat valleys on silicon across a broad range of incident angles when viewed by optical 3D microscopy. However, scanning electron microscopy (SEM) shows that these supposed craters are instead actually filled with amorphous black silicon-like structures that protrude away from the silicon surface. Black silicon is the generic name for nanostructured silicon with very high optical absorption properties that prior work has shown can be formed by fs-LA and other methods. By contrast, Gaussian fs-LA in atmosphere yields craters as observed by both optical 3D microscopy and SEM. Near ablation threshold fluences have been shown to yield these black silicon structures. The absorption range, absorption efficiency and shape of black silicon are directly affected by the experimental parameters used to form it. As shown in the figure below, the structures obtained from ablating silicon with flat-top fs-LA are irregular structures that deviate from the typical conical and/or cylindrical, partially ordered black silicon nanostructures previously reported in the literature.

AS-Contributed On Demand-109 Laboratory Based Hard X-ray Photoelectron Spectroscopy*, **Marcus Lundwall,*** Scienta Omicron, Sweden*;* *B. Giles,* Scienta Omicron

Hard X-ray photoelectron spectroscopy (HAXPES) is generally used to study core topics in condensed matter physics. However, with a worldwide increase in the number of HAXPES focused endstations, many other interest groups now recognize its broad appeal.In a HAXPES experiment 2-10 keV X-rays are used to excite photoelectrons to study the chemical environment and electronic structure of materials non-destructively. In contrast to standard XPS, HAXPES is more sensitive to what is beneath the surface. This makes it an ideal technique for studying structured samples that cannot be analyzed using traditional XPS. Bulk sensitivity means that realistic samples can be investigated without the need for surface preparation. Unfortunately, there are very few existing HAXPES systems. Most are predominantly located at synchrotrons, as the photoionization cross sections at high energies is small and necessitates large X-ray intensities.This work shows a new laboratory based HAXPES instrument capable of delivering monochromated 9.25 keV X-rays in a focused 30x45 μm^2 X-ray spot with energy resolution <0.5 eV. Systematic reference measurements demonstrate the system's capability. Application based results from various fields, including in operando measurements on devices and studies of energy related materials, are also presented.

AS-Contributed On Demand-112 Unravelling the Ion-Energy-Dependent Structure Evolution and Its Implications for the Elastic Properties of (v,Al)NThin Films*, **Soheil Karimi Aghda,*** Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany*; D. Music,* Department of Materials Science and Applied Mathematics, Malmö University, Sweden*; Y. Unutulmazsoy,* Leibniz Institute of Surface Engineering (IOM), Germany*; H. Sua, S. Mráz, M. Hans,* Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Schneider,* Chair of Materials Chemistry (MCh), RWTH Aachen University, Germany

Ion irradiation-induced changes in the structure and mechanical properties of metastable cubic (V,Al)N deposited by reactive high power pulsed magnetron sputtering are systematically investigated by correlating experiments and theory in the ion kinetic energy (E_k) range from 4 to 154 eV. Increasing (E_k) results in film densification and the evolution from a columnar (111) oriented structure at $E_k \leq$ 24 eV to a fine-grained structure with (200) preferred orientation for $E_k \geq$ 104 eV. Furthermore, the compressive intrinsic stress increases by 336 % to -4.8 GPa as $E_k$is increased from 4 to 104 eV. Higher ion kinetic energy causes stress relaxation to -2.7 GPa at 154 eV. These ion irradiation-induced changes in the thin film stress state are in good agreement with density functional theory simulations. Furthermore, the measured elastic moduli of (V,Al)N thin films exhibit no significant dependence on E_k. The apparent independence of the elastic modulus on $E_k$can be rationalized by considering the concurrent and balancing effects of bombardment-induced formation of Frenkel pairs (causing a decrease in elastic modulus) and evolution of compressive intrinsic stress (causing an increase in elastic modulus). Hence, the evolution of the film stresses and mechanical properties can be understood based on the complex interplay of ion irradiation-induced defecb generation and annihilation.

AS-Contributed On Demand-115 Monte Carlo Evaluation of Uncertainty in Hurst Exponents Computed from Power Spectral Analysis of Atomic Force Microscopy Images*, **Robert Chrostowski,*** Z. Li, F. Mangolini,* University of Texas at Austin

At sufficiently fine scales, all surfaces exhibit texture, which influences adhesive, optical, thermal, and mechanical properties of materials. Accurately predicting surface finish-property relationships is challenging because common summary statistics for surface texture (such as root mean square slope or curvature) can differ by even orders of magnitude *for the same surface* depending on the scale that is probed. A scale-invariant description can be obtained from Power Spectral Density (PSD) analysis of atomic force microscopy (AFM) height maps by computing the Hurst exponent (which is related to the fractal dimension). While estimation of Hurst exponents from PSDs is a common analysis technique widely used in many disparate fields (from contact mechanics to astronomy), few studies exploring the *accuracy* of this estimation exist. Here, we use a Fourier filtering algorithm combined with a novel approach to simulate typical AFM scan-line anisotropy to generate synthetic AFM topography images with *known* input Hurst exponent. A Monte Carlo approach is then used to evaluate the uncertainty, including both variance and *bias,* in Hurst estimation from PSDs across different hypothetical experimental approaches. Our analysis reveals that estimates of the Hurst exponent from images collected at a single scale are persistently biased in a scale-dependent fashion despite misleading convergence in variance. This bias can be reduced by combining images collected at least at three different scales across the range of scales accessible to AFM.

AS-Contributed On Demand-118 Spatially Resolved Molecular Compositions and Formation Mechanisms of Insoluble Engine Deposits Uncovered Using 3D OrbiSIMS*, **Max Edney,*** University of Nottingham, UK*; E. Wilmot, J. Reid, J. Barker,* Innospec Ltd., UK*; M. Alexander, C. Snape, D. Scurr,* University of Nottingham, UK

Formation of insoluble fuel deposits in internal combustion engine components is a major problem for the automotive industry and the wider population. Their formation results in reduced engine efficiency and higher emissions of particulates and other toxic pollutants, contributing to accelerated global warming and reduced air quality. These issues constitute major crises from an environmental and healthcare perspective.

Characterisation of deposits is a necessary first step in mitigating their formation. Previous attempts have used a range of techniques, providing elemental and/or basic structural information.[1] Time of flight secondary ion mass spectrometry (ToF-SIMS) differs from other techniques and illustrated *in situ* analysis of deposits at all depths using a sputtering beam and first showed that deposits are layered materials. But the technique offers a relatively low mass resolving power (10,000) and only elucidated small molecular fragments due to its high energy ion beam (Bi_3^+, 25 keV). Thus, there is a need for further work to provide a comprehensive, molecular, characterization of deposits in 3D.

Here we introduce the application of 3D OrbiSIMS (HybridSIMS, IONTOF GmbH)[2], with its superior mass resolving power (> 240,000), for characterising gasoline and diesel engine deposits.[3] Single beam Ar_{3000}^+ (20 keV) depth profiles and chemical images with a resolution of 20 µm over a 280 μm^2 area were acquired. We identified diagnostic molecular fragments including high mass polyaromatic hydrocarbons such as circumovalene (*m/z* 812) and lubricating additive species such as alkyl sulfonates ($C_{18}H_{29}SO_3^-$) in deposits for the first time. Assignments were then confirmed using MS/MS. Depth profiling with chemical imaging at interfaces illustrated where key species were localised and gave insight into how the layered structure of deposits arises. Combined results elucidate previously unconfirmed sources of contamination in the fuel stream and inform the design of next generation fuel additives to prevent deposit formation in gasoline and diesel engines, helping to improve air quality and reduce the impact of global warming.

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AS-Contributed On Demand-121 Nano Gas Cells: Multimodal Surface Analysis of Catalytic Processes at Elevated Pressures and Temperatures*, **Burcu Karagoz,*** Brookhaven National Laboratory*; J. Carpena-Núñez,* Air Force Research Laboratory*; Y. Zhu, D. Zakharov,* Brookhaven National Laboratory*; B. Maruyama,* Air Force Research Laboratory*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

Heterogeneous catalysis is usually analyzed by surface-sensitive techniques at ultra-high vacuum pressures and low temperatures using single crystals. However, catalysts used in industrial processes consist of metallic nanoparticles (NPs) and operate at near ambient pressures and high temperatures. To study heterogeneous catalysts in industrial conditions, we have developed nano gas cells. This cell allows studying solid-gas interfaces using anode-based ambient pressure X-ray photoelectron spectroscopy (APXPS) at temperatures up to 1300 °C and pressures exceeding the typical instrument limit of 10 mbar. This cell also enables multimodal transition electron microscopy (TEM) and APXPS experiments at pressures up to 1 mbar. We have tested the nano gas cell by covering DENS Solutions Wildfire nanochips with 100 nm Pd film with widely studied experiments such as CO adsorption/desorption reactions and Pd oxidation/reduction reactions. These known reactions confirm the gas cell temperature in the APXPS instrument. The growth of carbon nanotubes (CNTs) with metal oxide catalysts was also studied using both APXPS and TEM. This nano gas cell setup will be available to external users through the Center for Functional Nanomaterials (CFN) proposal system.

AS-Contributed On Demand-124 Plasma Modification of Lab Coat Fabrics for Improved Protective Clothing*, **Kimberly Hiyoto**, E. Fisher,* Colorado State University

With the widespread use of engineered nanomaterials in applications like healthcare, energy storage, sensing, and catalysis, secondary exposure from contaminated protective clothing is a major concern that is not widely studied.Although it is generally accepted that the fabric texture plays a vital role when determining nanoparticle (NP) adhesion and release on fabric, the impact of surface chemistry cannot be dismissed.Low temperature plasma treatment allows for the surface properties of the material to be tuned while the overall weave structure remains unchanged.This allows for direct comparison of the same fabric with differing surface properties to better elucidate how nanomaterials interact with these fabrics and if this behavior is influenced more by weave texture or surface chemistry.

Here, we describe plasma modification of four commercially available lab coat fabrics (100% cotton, polyester/cotton blend, polypropylene, and Tyvek®) and the resulting adhesion and release behavior with aluminum oxide NP, carbon black, and carbon nanotubes.Both C_3F_8 and $H_2O_{(v)}$ plasmas were used at relatively low applied powers to render the fabric more hydrophobic and hydrophilic, respectively.X-ray photoelectron spectroscopy indicates that C_3F_8 plasma treatment of all fabrics resulted in deposition of a thin fluorocarbon (FC) film with some contributions from the underlying material and $H_2O_{(v)}$ plasma treatment increased the amount of O on the surface by up to 10%.Contact angle goniometry confirmed the increase and decrease in hydrophobicity of the FC coated and $H_2O_{(v)}$ plasma treated samples, respectively when compared to the untreated material.Scanning electron microscopy images were used to characterize nanomaterial interaction following contamination and after vigorous shaking for both the untreated and plasma treated materials.With both the Al_2O_3 NP and the carbon black, the $H_2O_{(v)}$ plasma treated fabrics generally had the lowest initial attachment.In addition, differences between the untreated and plasma treated materials indicate the fabric texture is not the only property controlling NP adhesion and release.Results from imaging the same spot on some of the investigated fabric swatches (polypropylene and polyester/cotton blend) before and after shaking will also be discussed to directly demonstrate the potential for secondary exposure from these materials.Ultimately, better understanding of how nanomaterials interact with a variety of woven and nonwoven fabrics will allow for better safety recommendations and potentially designing more effective protective clothing.

AS-Contributed On Demand-127 Lab-Scale Hard X-Ray Photoelectron Spectroscopy (HAXPES): Application to Buried Interfaces in Device Technology*, **Pierre-Marie Deleuze**, E. Martinez, O. Renault,* CEA-Leti, France

X-ray Photoelectron Spectroscopy (XPS) is a powerful tool to study the electronic surface properties of materials. However, its low analysis depth remains a major limiting factor to study buried interfaces which properties are yet crucial in many applications. This limitation can be overcome using hard x-ray sources (HAXPES) thanks to the increase of the inelastic mean free path of electrons with increasing photon energy. Though HAXPES have been available at synchrotron facilities for many years, the recent advent of commercial laboratory instruments enables routine analysis with enhanced probing depth [1,2].

Here, we present the possibilities offered by a novel, Cr Kα (hν=5414.9 eV) lab-based HAXPES through several practical cases. In particular, we show that HAXPES can be appropriate to non-destructively probe buried interfaces in nanoelectronic devices. Among the examples, the potential of HAXPES is demonstrated through the investigation of Al_2O_3/GaN interfaces, which are of primary interest in the field of high-electron mobility transistors (HEMT). Results highlight that HAXPES is required to study realistic devices as the thickness of alumina plays important role on the structure properties. Furthermore, we discuss TiN/HfO_2 heterostructures intended for oxide-resistive random access memories (OxRAMs). The influence of a metallic Ti layer deposited at the interface is especially examined. Results reveal that the addition of a Ti layer promotes the reduction of hafnium oxide thus creating oxygen vacancies, which in turn greatly determine the device properties.

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AS-Contributed On Demand-130 XPS Depth Profiling of Metal-Halide Perovskites*, C. Clark,* Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.*; **Jennifer Mann**, B. Schmidt, K. Artyushkova, J. Newman,* Physical Electronics, Inc.*; E. Aydil,* New York University*; R. Holmes,* University of Minnesota,

The goal of an XPS depth profile is to obtain accurate identification of layer thicknesses and/or composition as a function of depth within film structures. Monatomic Ar^+ has been available for many years and is often the gun of choice for inorganic thin film profiling despite its issues with preferential sputtering, material migration, and chemical reduction that may occur thus altering the apparent profile of the analyzed material [1-3].

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years has expanded the types of materials that may be studied by depth profiling beyond that of inorganic thin films.Cluster type ion guns have shown successful depth profiling of polymer and organic materials as well as inorganic thin film structures while preserving the stoichiometry and chemical structures [4-6].

Organo-metal-halide perovskites are of interest due their promising application in solar cells where they have achieved efficiencies above 25% [7]. In this work, we present XPS depth profiles of single films of different metal-halide perovskites having an ABX_3 structure(A = MA - methylammonium or Cs, B = Sn or Pb, X = Br or I). Depth profiles using all three sputtering guns available on the PHI *VersaProbe* III - monatomic Ar, C_{60} and argon gas cluster (GCIB) - were obtained to determine the viability of each gun in maintaining both the stoichiometry and chemistry of the film as it was sputtered.

A more complex two-layer heterojunction of organo-metal-halide perovskites was also investigated using optimized ion sputtering conditions. This is a particularly well-suited system for XPS depth profiling due to the accessible thicknesses of the layers and the significant difference in chemistry of carbon and nitrogen in different organic A-site cation environments. Indeed, this difference is exploited to probe ion migration and mixing across perovskite interfaces.

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AS-Contributed On Demand-133 Characterization on ALD-functionalized Magnesium Borohydride Materials for Hydrogen Storage*, **Margaret A. Fitzgerald**,* Colorado School of Mines, Department of Chemistry*; N. Leick,* National Renewable Energy Laboratory*; K. Gross,* H2 Technology Consulting LLC*; S. Christensen ,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines, Department of Chemistry

Increasing energy demands and emissions require society to move towards more renewable and efficient energy carriers like hydrogen. However, development of effective methods of hydrogen storage and transportation is essential for the implementation of a hydrogen-based energy economy. Many materials can store hydrogen, including metal organic frameworks, activated carbons, and metal hydrides. Of these, metal borohydrides show promise as they have high gravimetric densities of hydrogen are potentially a more practical material for transportation[1]. One promising borohydride is magnesium borohydride ($Mg(BH_4)_2$, MBH), which with the addition of dopants (like titanium or fluorine),has potential to store hydrogen near room temperature at low-to-moderate pressures and at energy densities greater than either liquid or compressed hydrogen.[1] While MBH dopants are traditionally introduced mechanically, this work focuses on the characterization of MBH that has been doped using atomic layer deposition to introduce BN and TiN to tailor the deposited materials to a set of H2 storage targets. Understanding the complex chemical interactions between ALD precursors and the MBH requires a thorough characterization of the surface and bulk of as- received and ALD-functionalized materials. However, the air- and beam- sensitivity of MBH and particle heterogeneity of the as received and ALD-coated materials increases the challenges associated with characterization of this class of materials. This talk presents these challenges and presents the solutions developed in the characterization of the uncoated and coated MBH materials. Initial characterizations of these materials included temperature programmed desorption, surface area measurements, and scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectrometry (EDS) are used to understand differences in the ALD-functionalized materials. Furthermore, ex-situ identical location STEM combined with EDS are employed to understand the effect of dehydrogenation on morphology and chemical composition of the materials. This allows to distinguish the heterogeneity of the initial materials from that of the deposited ALD coatings. Changes in morphology and composition are quantified and correlated to the amount of H2 dehydrogenation, the surface area, and H2 cyclability allowing for assessment of these materials in terms of performance and cyclability.

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AS-Contributed On Demand-136 Use of Artificial Intelligence Techniques to Automate the Analysis of XAFS spectra*, **Jeff Terry,*** Illinois Institute of Technology

One of the major issues affecting the scientific community is reproducibility[National Academies of Sciences, Engineering, and Medicine, \textit{Reproducibility and Replicability in Science}, 2019] or more specifically the lack thereof. A second issue involves the quantity of experimental data being produced on a yearly basis[C. Wang, U. Steiner, and A. Sepe, Small 14, 1802291, 2018]. Both of these issues limit the utility of the data collected during the operation of the synchrotron radiation user facilities. This hurts the scientific community as there is a strong possibility that important new science is lost, forever locked up in un-analyzed data that a funding agency paid to collect. Whether data is lost due to inactivity or was improperly analyzed, the knowledge that is lost cannot be used to improve our understanding of the physical world. At worst, time is wasted trying to replicate incorrect conclusions[M. Linford, V. Jain, and G. Major, AVS66 Abstract Book, 72, 2019]. Ultimately, there is a limit on what humans will be able to accomplish without the assistance of computers. Even with the efforts to train more experts, the amount of data that can be collected from *in situ* chemistry measurements exceeds what a researcher can analyze without computer assistance. We have developed an analysis program that reduces the amount of human intervention needed to successfully conduct the analysis of extended x-ray absorption fine structure (EXAFS) data.

There are three problematic issues that we have observed over the years in the analysis of EXAFS spectra. The first involves the data reduction involved to obtain the analyzable interference data, χ(k). The proper adjustment of the background parameters to reduce the contribution of low R (short scattering path lengths) is very confusing to novice users. Second, the extraction of local atomic structure from theoretical standards is difficult as it relies on human users to identify both the compounds and the respective scattering paths from each that are present in the experimental data. Third, the speed at which EXAFS data can be collected allows for *operando* monitoring of chemical reactions[G. T. Whiting, F. Meirer, and B. M. Weckhuysen, XAFS Techniques for Catalysts, Nanomaterials, and Surfaces, 167, 2016]. Our machine learning tools that we have developing can be used to address these problematic areas of XAFS analysis.

AS-Contributed On Demand-139 ALD Overcoating for Hydrogenation and Dehydrogenation Catalysts*, **Staci Moulton,*** Forge Nano

While ALD has grown to be an essential and widely implemented technique in two-dimensional nanoscale device manufacturing, the innovative commercial development of applications for three-dimensional and porous materials have comparatively lagged. At Forge Nano, we recognize the criticality of enabling these ALD-assisted technologies for commercial applications, particularly in catalysis. We will demonstrate that ALD-overcoated catalysts, adding a metal-oxide top layer to a traditionally fabricated catalyst, enabled metal catalysts through targeted coating strategies for specific catalytic deactivation challenges. Our overcoat catalysts retain activity, physical stability in hydrothermal and thermal conditions, achieve improvements in selectivity, and significantly enhance lifetime. For hydrogenation of muconic acid to adipic acid the Al_2O_3 ALD-coated catalysts retain up to two-fold activity for Pd on TiO_2 support. Second, the Pd leaching from the catalyst was reduced by four-fold on the ALD-coated catalyst. The same Pd on TiO_2 catalyst with ALD-overcoat showed significant resistance to physical restructuring under thermal treatment conditions shown both by STEM-EDS elemental mapping and activity data for uncoated and ALD-overcoated catalysts. Thermal treatment, or catalyst regeneration cycles, reduced the active catalyst surface area by over 80% for the uncoated catalyst while the ALD-overcoated catalyst retained all its active surface area over 5 regeneration cycles. The benefits of ALD for catalysis are proving to be a fertile working ground for both active materials and overcoat applications.

AS-Contributed On Demand-142 The Deterioration Mechanism of Silicone Elastomer during Vacuum Casting of Polyurethane*, **Natalie Frese,*** Bielefeld University, Germany*; M. Wortmann,* Bielefeld University of Applied Sciences, Germany*; K. Viertel,* Bielefeld University of Applied Sciences,, Germany*; W. Keil,* Paderborn University, Germany*; A. Welle,* Karlsruhe Institute of Technology, Germany*; W. Hachmann,* Bielefeld University, Germany*; C. Schmidt,* Paderborn University, Germany*; B. Hüsgen,* Bielefeld University of Applied Sciences, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

The industrial production of prototypes made of polyurethane via silicone casting molds in the vacuum casting process is state of the art. The silicone molds show progressive deterioration, as the isocyanate component of the PUR casting resin diffuses into the silicone during processing, thus, limiting their service life [1]. Here, an in-depth investigation of the underlying chemical and physical mechanisms on a molecular level is presented. It has been shown that an anomalous diffusion process of diisocyanate into the silicone surface leads to the formation of interpenetrating polymer networks of polyurea derivatives in the poly(dimethylsiloxane) matrix [2]. The heterogeneous polymer system was examined in spatial resolution utilizing time-of-flight secondary ion mass spectrometry (ToF-SIMS), transmission electron microscopy (TEM), helium ion microscopy (HIM), atomic force microscopy (AFM), thermo-gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) as well as nuclear magnetic resonance spectroscopy (NMR).

[1]Wortmann et al., *ACS Omega6*(7), 4687-4695 (2021).

[2]Wortmann et. al., *ACS Appl Polym Mater* 2(11), 4719-4732 (2020).

AS-Contributed On Demand-145 Oxidation of Amorphous Metal Alloy Surfaces Studied Using Ambient Pressure X-Ray Photoelectron Spectroscopy*, **Pedro Alzaga,*** Oregon State University and HP Inc.*; J. Diulus, R. Addou,* Oregon State University*; W. Stickle,* HP, Inc.*; J. Jenkins, G. Herman,* Oregon State University

Amorphous metal thin films (AMTFs) are of growing interest due to their unique mechanical properties and chemical stability. AMTFs have an advantage over polycrystalline metal films due to the lack of grain boundaries which gives AMTFs added durability and relatively smoother surfaces. For this reason, AMTFs have been investigated as potential materials for a wide range of applications such as protective layers in microelectromechanical systems, coatings for biomedical tools, and as metal-insulator-metal tunnel diode electrodes. However, AMTFs are known to be structurally and chemically unstable at higher temperatures and therefore the thermal stability of these materials need to be closely studied. The present research is focused on the characterization of the thermal stability of a ternary AMTF with a composition of $Ta_{54}W_{27}Si_{19}$ using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Using AP-XPS allows the composition and oxidation states of the growing oxide layer to be measured *in situ* as the AMTFs are heated in varying temperatures and O_2 partial pressures. Experiments were run at O_2 partial pressures ranging from 10^{-4} to 10 mbar and temperatures ranging from 25 to 300° C. Spectra have been obtained at a relatively short time intervals, which made it possible to determine the rate of oxide growth in combination with calculations using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. Analysis of the AP-XPS data indicated an increase in the apparent oxidation activation energy for $Ta_{54}W_{27}Si_{19}$ compared to similarly prepared polycrystalline tantalum films, which results in slower oxide growth. The results also indicated that the Ta in TaWSi films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta_2O_5) layer on the surface.

AS-Contributed On Demand-148 High-Speed Analysis of Spectroscopic Ellipsometry Data Using Deep Learning Methods*, Yifei Li,* Massachusetts Institute of Technology*; H. Yu, I. Takeuchi,* University of Maryland, College Park*; R. Jaramillo,* Massachusetts Institute of Technology

As a high-precision and non-destructive measurement, ellipsometry is a powerful means to measure optical properties (*e.g.* refractive index) and characterize device processing (*e.g.* layer thickness). It would be particularly valuable in autonomous, closed-loop, high-throughput experimentation to develop new materials for integrated photonics. High-throughput experimental approaches require high-throughput data analysis methods to match, but ellipsometry data analysis using conventional machine learning (ML) methods of nonlinear regression is too slow. Solving the inverse problem of ellipsometry involves large numbers of parameters, but the parameter space and training time expand exponentially with the numbers of parameters. Hence, conventional ML methods make assumptions and compromise accuracy to reduce the number of parameters. This challenge is well addressed by deep learning (DL). The training efficiency of DL is exponential with the number of training data points, which counters the challenge of geometrically-large parameter spaces, making DL feasible in many cases for which conventional ML is infeasible. DL inference only involves matrix multiplication and a constant-time nonlinear function evaluation, which are orders-of-magnitude faster than nonlinear regression.

We construct and train a DL model to infer the optical properties of Ge-Sb-Te (GST) phase-change materials, deposited as thin films with a combinatorial composition gradients on SiO_2/Si substrates. In model testing, the mean-average-error (MAE) and standard deviation for the DL-inferred complex refractive index are 0.0329 and 0.0578 respectively. The DL method is five times more accurate than conventional human-directed non-linear fitting (benchmarked using simulated data), and 1,000 times faster (e.g. 700 ms vs. 30 min for analyzing experimental data from 177 unique compositions). We use DL ellipsometry to analyze the complex refractive index of 177 unique compositions in the GST system, and we and find that $Ge_{0.30}Sb_{0.27}Te_{0.43}$ has the optimal figure of merit for phase-change functionality in the 400-1000 nm wavelength range.

[1] A. G. Kusne, H. Yu, C. Wu, H. Zhang, J. Hattrick-Simpers, B. DeCost, S. Sarker, C. Oses, C. Toher, S. Curtarolo, A. V. Davydov, R. Agarwal, L. A. Bendersky, M. Li, A. Mehta, and I. Takeuchi, *On-the-Fly Closed-Loop Autonomous Materials Discovery via Bayesian Active Learning*, Nature Communications **11**, 5966 (2020).

AS-Contributed On Demand-151 Optimization of LLZCN/LiPF$_6$/PEO Solid-state Electrolyte for Energy Storage Application*, Samuel Danquah,* Norfolk State University*; C. Denize,* Norfolk Sate University*; J. Strimaitis, S. Pradhan, C. Bonner, M. Bahoura,* Norfolk State University

Solid-state electrolytes (SSEs) bring forth the chances to maximize the use of lithium metal anodes and intrinsically eliminate the safety concerns associated with flammable liquid electrolytes. The majority of SSE research has so far focused on increasing ionic conductivity and improving interfacial stability. Because ceramic electrolytes (LLCZN) have high conductivities but are fragile, and polymer electrolytes are easy to process but have low conductivities, we took the advantages of both by preparing a composite structure of these two materials. In this work, we investigate the effect of different proportions of the individual compounds towards the ionic conductivity, flexibility or both of composite solid-state electrolyte LLZCN/$LiPF_6$/PEO. Our results demonstrate significant progress towards all-solid-state electrolytes with good ionic conductivity for high-energy-density solid-state batteries. Furthermore, the electrochemical testing confirms that varying weight composition of the solid-state electrolyte has an effect on the cycling performance.

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AS-Contributed On Demand-157 Analysis of Thin Film Specimens Using ToF-SIMS Wedge Protocol, A Comparison with Depth Profiling*, Vincent Smentkowski,* *S. Goswami,* GE-GRC*; F. Kollmer, J. Zakel, H. Arlinghaus, D. Rading,* IONTOF GmbH, Germany

Depth profiling (1D or 3D) is often used to determine the depth distribution of species in thin films.An advantage of ToF-SIMS depth profiling is a full mass spectrum is saved at every volume element enabling 3D analysis of unexpected species; the analyst does not need to select the species at the start of the measurement.A disadvantage of ToF-SIMS depth profiling is the analyst needs to determine if they want to optimize the erosion and detection protocol for the collection of either the positive or negative ion fraction.MCs^+ analysis, where the region of interest is eroded using a Cs^+ ion beam and a Bi^+ cluster ion beam is used to perform positive ion analysis has been reported and enables the analysis of both positive ion (as Cs adducts) and negative ion (Cs_2 adduct) species in one depth profile measurement. Disadvantages of MCs^+ analysis include data complexity and for optimal performance, Xe/Cs co-sputtering is required.In 2011, Mao et.al. reported wedge sample preparation for ToF-SIMS analysis of thin layers using a home-built instrument [Dan Mao, Caiyan Lu, Nicholas Winograd, Andreas Wucher "Molecular Depth Profiling by Wedge Crater Beveling"; Anal. Chem. 83(16) (2011) 6410-6417doi:10.1021/ac201502w [https://dx.doi.org/10.1021%2Fac201502w]]; in 2018 IonTof added wedge preparation into their commercial instrument.

In this presentation we compare time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling of a multilayer thin film sample with ion images generated on a wedge cut.The benefits of both wedge preparation and multivariate statistical analysis (MVSA) are outlined.

AS-Contributed On Demand-160 Setting the Stage: Strain-Directed Metallization of Liquid Metals Using Surface Acoustic Wave Devices on Piezoelectric Substrates*, Brian Rummel,* *L. Miroshnik,* University of New Mexico*; A. Li, T. Sinno,* University of Pennsylvania*; G. Balakrishnan, S. Han,* University of New Mexico

In our previous work, surface acoustic wave (SAW) devices were fabricated on a GaAs (<u>100</u>) substrate to demonstrate the ability of Raman microscopy to image and characterize acoustic waves traveling on the surface of a piezoelectric substrate. We have adapted this research to study the effects of acoustic strain on the metallization of liquid indium on GaAs. SAWs are generated using a two-port interdigitated transducer (IDT) design, modified to produce standing waves within a 200 x 200 μm^2 window on the surface of the substrate. The standing SAWs produce surface stresses on the order 10^8 Pa. SEM/EDS analysis and AFM are used to characterize the diffusion behavior of the adatom species. Electrical device performance is recorded with a vector network analyzer, and surface displacements are measured with AFM and Raman microscopy. Experimental values are compared to simulations generated using COMSOL Multiphysics. Furthermore, we show preliminary results demonstrating the potential of increasingly complex IDT geometries to produce intricate diffusion patterns for quantum structures or single electron device fabrication.

AS-Contributed On Demand-163 Current Trends in XPS Data Analysis, Including Major Errors and the Most Common Elements and Materials Analyzed*, George Major,* Brigham Young University*; T. Avval, B. Moeini,* Brigham Young University*; A. Herrera Gomez,* CINVESTAV-Unidad Querétaro, México*; C. Easton, T. Gengenbach,* CSIRO, Australia*; W. Skinner,* Future Industries Institute, University of South Australia, Australia*; D. Baer,* Pacific Northwest National Laboratory*; M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most widely used method for chemically analyzing surfaces, with applications in numerous areas of research and technology. In part, the popularity of XPS is due to the large amount of chemical information it derives from the surface, including chemical compositions, chemical and electronic states of elements, and elemental bonding. Extraction of this information, however, is not always straightforward. Various articles and guides have recently been published that teach and illustrate good methods for interpreting and fitting XPS data. In conjunction with these guides, some of us have recently surveyed 407 publications from three major journals that show XPS to gain greater insight into how XPS is being used, e.g., whether there are mistakes or errors in XPS analysis, which elements are the most commonly fitted, and which are the most problematic. A committee of international experts was formed to review the peak fitting in these papers and to rank the results vis-à-vis a list of common errors in XPS peak fitting. Error classification ranged from minor errors that have little impact on the interpretation of the results, such as plotting the spectrum against convention (with binding energy increasing to the right), to major errors that call into question the interpretation of the data or even of the entire study, such as not properly constraining the full-width half maxima values of fit component peaks. We found that 65% of the publications we analyzed included fitted XPS data. Of this fitted data, 40% showed major errors. The most popular elements that were fitted/shown are carbon, oxygen, nitrogen, sulfur, and titanium. In the papers we reviewed, the most common form of carbon (C 1s) that is analyzed is sp^2 carbon, and the most common form of oxygen (O 1s) that is analyzed is from inorganic oxides. These findings should help guide and direct further efforts for new XPS tutorial material.

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