Atomic Scale Processing Focus Topic
Room 317 - Session AP+2D+AS+EM+PS+SS+TF-MoM

Area Selective Processing and Patterning

Moderators: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, **Adrie Mackus**, Eindhoven University, Netherlands

8:20am **AP+2D+AS+EM+PS+SS+TF-MoM-1 Imperfectly Perfect Materials and/or Processes as a Route for ASD*, Christophe Vallee,*** SUNY POLY, Albany*; M. Bonvalot, M. Jaffal, T. Yeghoyan,* University Grenoble Alpes, LTM, CNRS, France*; N. Posseme, R. Gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

In recent years, many strategies have been presented to selectively deposit a material on a specific surface (area selective deposition), or space direction (topographically selective deposition). Whatever the selective process developed to this end (inherent delay, surface inhibition, surface activation, super-cycles...), it is expected that a perfect material is perfectly deposited on the surface at stake. However, this most often implies that some imperfect material is thereby deposited on surfaces where no growth is expected. Taking this logic a little further ahead, we can even imagine that it may not be at all necessary to develop perfect ALD processes to achieve ALD-based selective deposits.

In this presentation, we will show how imperfect ALD processes can be developed by working out of the ideal precursor ALD window or regime, to adequately lead to ASD processes. We will also show that the requirements of an ideal growth inhibition of no-growth surfaces can be successfully circumvented for ASD processes. Indeed, the simultaneous deposition of a same material on two differing substrates can lead to inherent discrepancies in the materials quality, that can be advantageously taken into consideration in the development of a localized bottom-up growth strategies by adding a selective etching step.

9:00am **AP+2D+AS+EM+PS+SS+TF-MoM-3 Area Selective Deposition on EUV Photoresist*, Rosanna Robert,*** SUNY College of Nanoscale Science and Engineering*; H. Frost, K. Lutker-Lee,* TEL Technology Center, America, LLC, USA*; C. Vallée,* SUNY College of Nanoscale Science and Engineering

Area selective deposition (ASD) is a key process required for the next generation of nanotechnology. ASD utilizes surface chemistry and reaction modifications to promote growth on one of two different materials. When applying an ASD process to a patterned wafer with both materials exposed, we can selectively grow a film on one surface while blocking growth on the other surface (known as the nongrowth area). One application for ASD is ultra-thin extreme ultraviolet (EUV) photoresist repair to enable continued pitch scaling in the Back End of Line[1]. Pattern transfer fidelity depends on initial line edge roughness (LER) and line width roughness (LWR) values of the EUV resist. Moreover, local critical dimension uniformity (LCDU) for <30 nm critical dimension hole patterning also varies with the initial resist thickness[2]. In this project, we propose to develop an ASD on EUV resists before or alternatively during an etch process to improve LCDU and LER/LWR; in this case, the ASD is used as a corrective step.

To develop an ASD process that is relevant to device manufacturing, we only consider the gases present on a plasma etch chamber as precursors for ASD. We utilize the plasma assistance of the etch chamber to develop an ASD process by Plasma enhanced chemical vapor deposition, rather than by the more commonly exploited atomic layer deposition. This is more challenging since radicals from precursor dissociation are known to be highly reactive on the surface. However, it was recently demonstrated the selective PECVD of a silicon film on SiON surfaces using SiF4/H2 plasma[3].

In this presentation, we will demonstrate ASD by PECVD on SnOx (a EUV resist material) vs SiO-based materials (underlayer) in a 300 mm plasma etch tool, and the impact of plasma precursors and parameters on selectivity. We will show that we can selectively deposit film on SnOx. Results on full wafers and patterned samples will be presented. Thanks to the use of an in-situ plasma diagnostic, such as optical emission spectroscopy, as well as of ex-situ surface diagnostics such as X-ray photoelectron spectroscopy and scanning electron microscopy, we will discuss the mechanisms inherent to the selective growth and discuss the impact of chemistry of neighboring materials and pattern density.

1 J.Church, "Plasma based ASD for EUV resist defectivity reduction and process window Improvement" *AVS* (2021) Nov 2020

2 B. Vincent et al, Proc. *SPIE 11323,* "Extreme Ultraviolet (EUV) Lithography XI,"1132326 (23 Mar 2020)

3 G. Akiki et al, "Origin of area selective plasma enhanced chemical vapor deposition of microcrystalline silicon," *J. Vac. Sci Technol.A* 39 (2021) 013201

9:20am **AP+2D+AS+EM+PS+SS+TF-MoM-4 Impact of Post-Exposure Treatments on TMSDMA-Passivated SiO_2 Surfaces*, Anthony Valenti,*** *C. Vallée, C. Ventrice,* SUNY Polytechnic Institute, Albany*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC

As the scale of semiconductor devices continues to shrink, conventional approaches to fabrication such as photolithographic patterning are becoming limited in their ability to provide the precision and resolution required for smaller and smaller features. Over the last several years, a bottom-up and self-aligned patterning technique known as area-selective deposition (ASD) has been explored. With this technique, the deposition process is manipulated in such a way as to only promote growth on one type of surface on a patterned substrate. This is typically achieved by inhibiting specific surfaces through the selective chemisorption of molecules that are inert to the reactants used for growth of the material of interest. Aminosilane precursors such as *N*-(trimethylsilyl)dimethylamine (TMSDMA) are of recent interest due to their potential use in area-selective atomic layer deposition (AS-ALD). With their strong selective chemisorption on SiO_2 surfaces versus Si and non-oxidized metal surfaces, these precursors can be used to block deposition of metals on SiO_2 while not inhibiting growth on Si or metal surfaces. For aminosilanes to be used as inhibiting precursors in AS-ALD, the resulting layer must maintain its passivation throughout a dozen or more ALD cycles. This study investigates the impact of various common ALD co-reactant/post-exposure treatments on SiO_2 surfaces passivated via exposure to TMSDMA, including ozone exposure, H_2 plasma treatment, and H_2 plasma treatment followed by H_2O vapor exposure. This project also explores using a second inhibitor dosing via NF_3 plasma treatment in order to fluorinate any nucleation sites left vacant on the SiO_2 surface after TMSDMA exposure. These treatments were conducted on samples of TMSDMA adsorbed on Si(100) substrates with 1000 Å thick thermal oxide surfaces. Water contact angle measurements were taken of each sample to determine relative surface passivation of each sample and to monitor temporal degradation of the surfaces over a timescale spanning weeks. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to determine the chemical state of each surface. Temperature programmed desorption measurements were conducted to assess the relative coverage of the inhibiting film on each sample and their stability at higher temperatures.

9:40am **AP+2D+AS+EM+PS+SS+TF-MoM-5 Area-Selective ALD Using Small Molecule Inhibitors of Different Sizes: Single and Sequential Inhibitor Dosing*, Pengmei Yu,*** *M. Merkx, I. Tezsevin,* Eindhoven University of Technology, Netherlands*; P. Lemaire, D. Hausmann,* Lam Research Corp.*; T. Sandoval,* Federico Santa María Technical University, Chile*; W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Due to the continuous scaling of semiconductor device features, area-selective atomic layer deposition (ALD) is gaining attention for enabling bottom-up fabrication with atomic-scale control. Area-selective ALD can be achieved by surface deactivation of the non-growth area using inhibitor molecules. Small molecule inhibitors (SMIs) are of great interest due to the vapor-phase application and corresponding industrial compatibility.[1] Our previous work established that SMIs block precursor adsorption by a combination of chemical passivation of surface sites and steric shielding.[2] In this contribution, we compared three SMIs of different sizes for SiO_2 inhibition on the Al_2O_3 surface, namely acetic acid (HAc), acetylacetone (Hacac), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), and explored sequential dosing of two different SMIs to increase the overall inhibitor packing.

We first focused on the use of a single SMI and studied how the size influences their performance. By in-situ spectroscopic ellipsometry and infrared spectroscopy studies, it is observed that using either a smaller (HAc) or a larger (Hthd) SMI than Hacac[3] could improve SiO_2 ALD inhibition. Density functional theory and random sequential adsorption simulations were performed to further understand experimental findings. We found that although both steric shielding and chemical passivation are required for effective precursor blocking by SMIs, neither of them plays a dominating role. As compared to Hacac, HAc performs better due to its small size, yielding denser packing and thereby a higher degree of chemical passivation. Hthd on the other hand, benefits from its bulkiness, resulting in a higher contribution from steric shielding.

In an effort to achieve a higher selectivity, we explored whether sequentially dosing of two different SMIs can lead to higher surface coverage and deactivation. It is found that enhanced precursor blocking of 98.4 ± 0.2 % could be achieved by dosing HAc and Hthd sequentially, which is higher than either 96.0 ± 0.6 % by Hthd or 97.0 ± 0.5 %by HAc solely. Results for various combinations of inhibitors and sequences will be presented.

In summary, this work illustrates that varying the size of SMIs could bring benefits from either higher steric shielding or chemical passivation components for improved precursor blocking performance. In addition, it is demonstrated that combination of SMIs could potentially be an effective strategy for achieving higher selectivity.

[1] A.J.M. Mackus *et al.*, Chem. Mater. 31, 2 (2019).

[2] M.J.M. Merkx *et al.*, J. Phys. Chem. C 126, 4845 (2022).

[3] M.J.M. Merkx *et al.*, J. Vac. Sci. Technol. A 39, 012402 (2021).

10:00am **AP+2D+AS+EM+PS+SS+TF-MoM-6 Role of Catalytic Surface Reactions During Area-Selective Tan ALD for Precursor Blocking Using Aniline Molecules***, **Marc Merkx**[1], I. Tezsevin, P. Yu, R. Heinemans, R. Lengers, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Federico Santa Maria Technical University, Chile

The semiconductor industry is running into significant issues regarding RC-delays in state-of-the-art interconnect structures. A solution is to selectively deposit the transition metal nitride diffusion barrier on the dielectric via sidewalls but not at the bottom, known as a bottomless barrier structure.[1]. In this contribution, area-selective TaN ALD is investigated using aniline as a small molecule inhibitor (SMI),[2] with the focus on studying the catalytic surface reactions that take place on the metal non-growth area after aniline adsorption.

Area-selective TaN ALD was achieved using a three-step (i.e. ABC-type) ALD cycle using: (A) aniline as SMI, (B) tert-butylimidotris(dimethylamino)tantalum (TBTDMT) as the precursor molecule, and (C) an Ar-H_2 plasma as the co-reactant. This process was found to selectively deposit TaN on dielectric surfaces (e.g. Al_2O_3 and SiO_2) considering the metal surfaces (e.g. Co, Ru) as non-growth area. It was observed that the selectivity of the process is strongly dependent on the employed substrate temperature. At 175 °C only ~1 nm TaN can be deposited selectively, whereas by raising the substrate temperature to 300 °C ~3 nm of selective TaN growth was achieved on Al_2O_3, with respect to Ru as the non-growth area.

An explanation for the strong temperature dependence for the selectivity of this process could be the catalytic reactivity of the metal non-growth area. For example, through density functional theory (DFT) calculations, it was found that aniline can undergo a hydrogenolysis reaction on transition metal surfaces, where the amine group splits off as NH_3 while benzene remains adsorbed on the surface. This reaction eliminates the NH_2 groups from the surface that could otherwise interact with incoming precursor molecules.[3] Experimental and simulation results will be presented to provide insight into the role that catalytic surface reactions play during area-selective ALD on metal surfaces.

[1] Merkx et al., Atomic Limits **7**, (2022) https://www.atomiclimits.com/2022/04/18/

[2] Merkx et al., Chem. Matter **32**, 7788-7795 (2020)

[3] Merkx et al., Chem. Matter. **32**, 3335-3345 (2020).

10:40am **AP+2D+AS+EM+PS+SS+TF-MoM-8 AVS Russell and Sigurd Varian Awardee Talk: Sequential Application of Two Inhibitors to Achieve Area-Selective Atomic Layer Deposition of Dielectric on Metal***, **Tzu-Ling Liu**[2][3], M. Harake, S. Bent,* Stanford University

Area-selective atomic layer deposition (AS-ALD), which provides a bottom-up approach to fabricate patterned structures, has been considered as a prospective solution to overcome the challenges in current semiconductor manufacturing processes. To enable more applications of AS-ALD, it is critical to expand the AS-ALD toolbox to different types of surfaces. Previous studies have successfully demonstrated selective deposition of dielectrics on the dielectric (DoD) regions of metal/dielectric patterns using alkanethiols and phosphonic acids as the inhibitors for metal surfaces. However, doing the reverse pattern transfer, i.e., selective deposition of dielectrics on the metal (DoM) regions, is less well-investigated because selective inhibitor deposition on dielectric over metal is more challenging. Taking organosilane, a common inhibitor choice for dielectric surfaces, as an example, it can also adsorb on metal substrates when native metal oxide is present. Hence, it is important to develop a strategy to protect metal surfaces from the adsorption of organosilane inhibitors for achieving AS-ALD of DoM.

In this work, we demonstrate a two-step strategy to achieve selective deposition of DoM by using two different SAMs with orthogonal surface chemistry, i.e., one SAM preferentially adsorbs on the metal, which serves as a protector to prevent the adsorption of the other SAM onto the metal, and the other primarily adsorbs on the dielectric, which serves as an inhibitor for AS-ALD. We sequentially perform dodecanethiol (DDT) deposition on Cu surfaces, followed by octadecyltrimethoxysilane (OTMS) deposition on SiO_2 surfaces. Since the Cu surfaces are protected by DDT in the first step, OTMS selectively forms a well-packed self-assembled monolayer (SAM) only on SiO_2. With this strategy, we demonstrate AS-ALD of ZnO and Al_2O_3 on Cu (growth surface) over SiO_2 (non-growth surface) after applying a thermal step to selectively remove DDT protector from Cu. The blocking results show that selectivity > 0.9 can be maintained after 35 cycles of ZnO ALD (corresponding to 5.6 nm of ZnO on a reference native SiO_2-covered Si substrate) and 15 cycles of Al_2O_3 ALD (corresponding to 1.4 nm of Al_2O_3), respectively, using this sequential two-step SAM process. Our study helps expand the selective deposition toolbox and provide more possible applications for AS-ALD in next generation electronic devices.

11:00am **AP+2D+AS+EM+PS+SS+TF-MoM-9 Carborane Self-Assembled Monolayers for Area-Selective Deposition***, **Michelle Paquette**, R. Bale, R. Thapa, S. Pinnepalli,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. An expanded palette of ASD materials and processes is needed. Boron carbide (BC) has been demonstrated to be a compelling candidate for low-*k* dielectric, etch stop, diffusion barrier, and patterning-assist layers, due to its robust electrical, mechanical, and chemical properties, as well as unique etch chemistry. The molecular carborane precursor is of interest for BC-based self-assembled monolayers (SAMs). This is a symmetric twelve-vertex molecule, with many available and typically sublimable derivatives. For SAM applications, carborane stands out in that its 3D symmetry allows for the formation of well-ordered layers, and the termination of its vertices by labile H atoms allows for cross-linking with a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam). Carborane SAMs can conceivably fulfill various roles in ASD schemes, including as an intrinsically selective functional dielectric layer (e.g., diffusion barrier), sacrificial layer (e.g., hard mask), direct-writeable layer, or blocking layer to facilitate the selective deposition of other materials. We describe progress in the deposition and characterization of carborane SAMs toward the development of a range of ASD schemes and applications.

11:20am **AP+2D+AS+EM+PS+SS+TF-MoM-10 Peter Mark Memorial Award Talk: Reactive Inhibitory Chemistries for Area Selective Depositions and Their Application in Back End of the Line Processes***, **Rudy Wojtecki**[4],* IBM Almaden Research Center **INVITED**

Area selective depositions (ASD) describe self-aligned processes where the chemical contrast of surfaces are exploited to selectively grow a film. ASD can be applied to a variety of fabrication schemes to improve tolerance to overlay errors in fully aligned via schemes or achieve device performance improvements by reduce resistance between interconnect levels in barrier-less contacts that reduce stage delay. While ASD processes are accessible through a variety of methods – differences in surface reactivities between materials, self-assembled monolayers (SAMs) and small molecule inhibitors, to name a few – reactive organic inhibitors and their application in ASD processes will be described. Reactive inhibitor compositions can be selectively deposited on a metal portion of a pre-pattern surface, then undergo (i) a crosslinking reaction or (ii) further chemical transformations used to grow an inhibitory film to a desired thickness. Crosslinking of a monolayer film for ASD was demonstrated with the introduction of diyne moieties into a SAM composition, which is crosslinked under either UV or thermal treatment. These crosslinked monolayers were found to enhance selectivity in an ASD process and reduce defects on patterned substrates.

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[1] **2021 TFD James Harper Awardee**

[2] **TFD James Harper Award Finalist**

[3] **AVS Russell and Sigurd Varian Awardee**

[4] **Peter Mark Memorial Award Winner**

With synthetic modifications to increase the length of the SAM, further reductions in defectivity was achieved as well as the ASD of TaN. Electron beam irradiation of aliphatic moieties are also known induce crosslinking. With the use of hydroxamic acid head groups the chemical contrast between exposed (crosslinked) and non-exposed regions could be significant enough to enable a patternable ASD process where, as the crosslink density increased the selectivity of the monolayer is further improved. These SAM chemistries require solution-based coating methods but the concept of a crosslinkable inhibitor could also be translated to a vapor phase process, demonstrated with propargyl amine and vinyl pyridine. To tailor inhibitor thickness in strategy (ii) chemically reactive surfaces were exploited where monomers are selectively attached to a metal surface then polymers grown in an area selective manner with tailorable thicknesses, demonstrated with a polynorbornene and poly(vinylpyridine). This tailorable thickness presents several advantages over monolayers – such as enabling ASD on patterns with topography (sharp corners & bends) or the control of lateral overgrowth. These reactive inhibitory chemistries demonstrate an inhibitory chemistry strategy for ASD and their use in back end of the line applications such as fully aligned via, barrier-less contacts or zero-line end extensions.

Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-MoM

Probing Surface and Interface Structure with X-ray Photoelectron Spectroscopy: In Memory of Charles Fadley

Moderators: Gregory Herman, Oregon State University, **Theva Thevuthasan**, Pacific Northwest National Laboratory

9:00am **AS+LS+RE+SS-MoM-3 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane***, **Trevor Willey**, J. Lee,* Lawrence Livermore National Laboratory*; D. Brehmer, O. Paredes Mellone,* SLAC National Accelerator Laboratory*; L. Landt,* Lawrence Livermore National Laboratory*; P. Schreiner, A. Fokin, B. Tkachenko,* Institute of Organic Chemistry, Justus Liebig University, Germany*; A. de Meijere, S. Kozhushkov,* Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany*; T. van Buuren,* Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some fundamental saturated carbon cage compounds. Adamantane, C10H16, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C10H16 isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)12, and cubane, (CH)8, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C–C σ* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octadedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)x. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C-C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

9:20am **AS+LS+RE+SS-MoM-4 Composition and Thermal Stability Analysis of Passive Films on NiCr and NiCrMo Alloys***, **Keithen Orson**, A. Costine, E. Romanovskaia, J. Scully, P. Reinke,* University of Virginia

Ni-Cr based super-alloys are important because of their corrosion resistance, which derives mainly from a thin passive layer of chromia (Cr_2O_3). During aqueous corrosion, a complex surface layer containing $Ni(OH)_2$, $Cr(OH)_3$, and Cr_2O_3 forms whose chemistry and structure are still subject of discussion. Our work is designed to study how non-equilibrium growth of the passive layer during aqueous corrosion affects the properties of the passive layer. We apply a range of electrochemical conditions to two alloys - Ni22wt%Cr, and Ni22wt%Cr6%Mo. Alloys are processed in pH 4 aqueous chloride solution. The electrochemical reaction step uses high or low current density (100-0.1 nA/cm^2) to achieve fast and slow passive layer growth that is far or near equilibrium, respectively. The second step was a 10 ks potentiostatic hold at +0.2V. Electrochemical processing was followed Angle-Resolved X-Ray Photoelectron Spectroscopy (ARXPS) analysis to characterize the oxide and hydroxide chemistry of the passive layer and underlying alloy. Annealing to 400 °C served as a proxy to assess the passive layers stability, which we propose is related hydroxide network connectivity and pitting resistance. In as-prepared samples, Ni and Cr hydroxides are dominant in the passive layer, while chromia and $Cr(OH)_3$ are the dominant species at elevated temperatures. The underlying alloy tends to be moderately enriched in Cr. Under all conditions and temperatures, Cr is present as a mix of oxide and hydroxide with the oxide dominating at higher temperatures. In contrast, $Ni(OH)_2$ is detected at low temperatures, but no NiO is observed. For molybdenum-containing alloys, MoO_x and Cr_2O_3 coexist until MoO_x is reduced at T>300˚C. Continuous XPS spectra taken during annealing indicate smooth transitions between hydroxide and oxide visible in the O1s and C2p3/2 peak shape, while for Mo 3d3/2 and Ni2p3/2 peaks narrow transition regions for reduction are identified. Oxide thickness decreases with increasing temperature due to oxide loss from reduction and volatilization. The fast and slow growth on Mo-containing alloys without a subsequent potentiostatic hold produced a marked difference in oxide thickness. Molybdenum content affects multiple characteristics of the passive layer, including thickness, layering, and chromia content. Our work demonstrates how differing preparation conditions affect the chemistry and layering of NiCr and NiCrMo alloys. These results will be interpreted in the context of passive film performance and can ultimately be used to design alloys for optimal corrosion resistance.

9:40am **AS+LS+RE+SS-MoM-5 Reversible Changes in Surface Charging and Surface Oxide of $NiFe_2O_4$ Thin Films: A Temperature Dependent X-Ray Photoemission Study***, **Arjun Subedi**, D. Yang, X. Xu, P. Dowben,* University of Nebraska-Lincoln

We have observed large binding energy shifts in temperature dependent X-ray photoelectron spectroscopy (XPS) of the $2p_{3/2}$ core levels of both Ni and Fe atoms in nickel ferrite ($NiFe_2O_4$) thin films grown on Al_2O_3. The binding energies of the core levels were found to be sensitive to photovoltaic charging. The apparent binding energies decreased by more than 5 eV for both core levels when the temperature was increased to 510 K from room temperature. This is evidence of large surface charging of the sample and indicative of insulating behavior at lower temperatures. The XPS spectra at higher temperatures were observed to be different from that at lower temperatures, suggesting a different surface oxide at higher temperatures. When temperature was lowered from 510 K to room temperature, the changes in surface charging and nature of the surface oxide were reversible. We conclude that the nature of the surface oxide is temperature dependent.

10:00am **AS+LS+RE+SS-MoM-6 The Reproducibility Crisis in Science as Manifested in X-Ray Photoelectron Spectroscopy (XPS). What's Been Done, and What's Being Done About It?***, **Matthew Linford**,* Brigham Young University*; D. Baer,* PNNL*; G. Major,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. Conventional XPS probes 5 - 10 nm into surfaces, revealing both the atomic compositions and chemical states of the atoms at surfaces. During the past few decades, there has been a significant increase in the use of XPS worldwide, both in the number of papers published that show XPS data and in the number of new XPS systems being sold. However, the world appears to have created new XPS instruments faster than XPS experts. Indeed, a recent paper suggested that about 40% of the XPS peak fitting reported in the scientific literature is deeply flawed (see *J. Vac. Sci. Technol. A***2020**, *38*, 061204). An anecdotal report suggests that the XPS peak fitting in submitted manuscripts is even worse. In this talk, we discuss some of the efforts that are being made to address the reproducibility crisis in science vis-a-vis XPS and surface analysis in general. These efforts include a collection of guides on XPS that was recently published in JVST, a second set of guides to JVST that is currently accepting submissions, a set of guides being written to Applied Surface Science Advances that is also currently accepting submissions, and 'XPS Insight Notes' that will be accepted by Surface and Interface Analysis. These latest two sets of guides will accept papers on any surface analytical technique. It is hoped that by providing useful guidance on XPS and other surface analytical methods, these efforts will improve the quality of data collection and analysis that is appearing in the surface literature. This talk will also discuss common errors in XPS peak fitting in the literature and ways to fix them.

10:40am **AS+LS+RE+SS-MoM-8 Study of Surface Oxides on $Pt_3Ni(111)$ and $Pt_3Co(111)$ using Ambient Pressure XPS*, Bongjin Simon Mun,*** Gwangju Institute of Science and Technology, Republic of Korea **INVITED**

Utilizing AP-XPS, the surface chemical states of $Pt_3Ni(111)$ and $Pt_3Co(111)$ is examined under CO oxidation condition. Under elevated oxygen pressure, the presence of surface segregation of transition metals is clearly observed in AP-XPS. Also, with AP-STM, the formations of nanostructured transition-metal oxides are confirmed during the segregation. As CO oxidation occurs, the interfacial oxygens on the nanostructured metal oxides display unique chemical reactivity. Difference between Pt_3Ni and Pt_3Co alloys surface will be presented.

11:20am **AS+LS+RE+SS-MoM-10 Probing the Oxidation Chemistry of TRISO Nuclear Fuels Using Depth Profiled XPS and Ambient Pressure XPS*, Jeff Terry,*** Illinois Institute of Technology

While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, an additional use is possible as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with (PES) has been that it has historically been an technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H_2O at temperatures of 500 C using an ambient pressure photoemission system. In addition, we have grown multilayer SiC/ZrN/C systems designed to protect the environment from silver release. We will report on the corrosion chemistry of the SiC, ZrN, and C layers as measured using ambient pressure photoemission. Finally, We can also compare this to samples oxidized under high pressures of water and then measured with sputter-depth profiled conventional XPS measurements. These measurements help us to understand the potential failure modes of accident tolerant nuclear fuels.

11:40am **AS+LS+RE+SS-MoM-11 Environmental X-ray Photoelectron Spectroscopy Study of Catalyst-Ionomer Interactions in Polymer Electrolyte Membrane Fuel Cells*, Jayson Foster,*** *S. Zaccarine, M. Dzara,* Colorado School of Mines, USA*; C. Baez-Cotto,* National Renewable Energy Laboratory*; S. Kim,* Colorado School of Mines, USA*; M. Batool, J. Jankovic,* University of Connecticut*; M. Ulsh, S. Mauger,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines, USA

Proton exchange membrane fuel cells (PEMFCs) are an important technology providing on-demand energy without contributing to greenhouse gases. High demand for this technology requires scaled-up fabrication of PEMFC catalyst layers (CLs), thus motivating studies that relate catalyst chemistry and morphology to processing parameters and performance characteristics. Currently, interfacial interactions between catalyst and ionomer are not well understood fundamentally, including the evolution of this interface under humidified conditions.

Environmental X-ray photoelectron spectroscopy (EXPS) is a highly surface-sensitive technique primed to provide information into the surface properties of CLs and further improve understanding of interfacial interactions among the catalyst, support, and ionomer. Although Nafion ionomer is inherently susceptible to X-ray degradation, XPS can be used effectively through a modified acquisition strategy developed previously in our group. In this work, EXPS was used to probe CLs using a series of electrodes prepared by a Mayer rod coating method. The catalyst-ionomer interface was investigated as a function of carbon support material, loading of the Pt catalyst on the support, and ionomer content in the catalyst ink. Surface information was acquired using *ex situ* and *in situ* XPS to emphasize this technique's capabilities at probing ionomer interactions and their evolution in a humidified environment. Scanning transmission electron microscopy (STEM) was used to visualize distribution of Pt nanoparticles on support, relating catalyst and support properties to their surface behavior while integrated with ionomer. Furthermore, scanning electron microscopy (SEM) and STEM imaging in combination with energy-dispersive X-ray spectroscopy (EDS) mapping of electrode cross-sections were utilized to visualize distribution of ionomer and Pt in the CL to further assist with interpretation of EXPS data. Results from this dataset emphasize the strength of this technique to study complex interfaces in PEM catalyst layers motivating further work expanding to other catalysts and ionomers.

Biomaterial Interfaces Division
Room 318 - Session BI+AS+PS-MoM

Biomolecular Interfaces and Underwater Adhesion

Moderator: Morgan Alexander, University of Nottingham, UK

8:20am **BI+AS+PS-MoM-1 Supported Lipid Bilayers as Model Systems to Understand Molecular Interactions at Complex Solid/Liquid Interfaces*, Pierluigi Bilotto,*** Centre for Electrochemistry and Surface Technology, Austria*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria

Generating a detailed molecular understanding of complex, simultaneous inter actions at reactive and/or dynamic solid|fluid interfaces is a challenge across disciplines, and has intrigued researchers for decades.[1, 2] Whether it is, for example, in medical adhesives, friction of articular cartilage,[3] or the adhesion of organisms in seawater,[2] complex macroscopic properties at crowded biologic solid|liquid interfaces are mediated by large numbers of individual nanoscale interactions.[4] Exactly this complex competition and molecular structuring at interfaces are central to a multitude of interfacial phenomena, such as membrane transport,[5] membrane conductance, [6,7] cellular adhesion [8] and adhesion regulation in the marine environment. [9]

In our previous works, we characterised a lipid-based model system (LMS) in terms of its stability and bending properties by employing atomic force microscopy and surface forces apparatus. [10] Then, we further modified its outer face with amine-terminating polymers to investigate the specific electrostatic interaction between the amine and a negatively charged mica surface. Then, we examined how interaction forces are affected by the electrolyte concentration, funding a direct exponential like decay between adhesion and electrolyte concentration. Specifically, we found a decrement of 90% in adhesion in a 1M sodium chloride environment. These fundings suggested the presence of a competing mechanism which was confirmed by a kinetic model at the interface involving two competing Langmuir isotherms. Finally, we could estimate ion/surface interaction energies from the experimentally recorded interaction force measurements.[11]

In the talk we will discuss these works and present the new research opportunities coming out from these results.

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8:40am **BI+AS+PS-MoM-2 Recombinant Lubricin Improves Anti-Adhesive, Wear Protection and Lubrication of Collagen II Surface**, *H. Yuan,* Tianjin University, China*; **Laura Mears,*** Vienna University of Technology, Austria*; R. Su,* Tianjin University, China*; M. Valtiner,* Vienna University of Technology, Austria

Lubrication in articular joints is regulated by a number of biomolecules including the collagen of the cartilage, lubricin and lipids in the synovial fluid. Camptodactyly-arthropathy-coxa vara-pericarditis syndrome (CACP) is a joint disease, which causes a lack of lubricin, leading to failed lubrication as well as abnormal deposition at cartilage surfaces. Injection of recombinant lubricin (R-LUB) is a promising way to treat the disease. Here, the protein adsorption and lubrication behavior of type II collagen (COL II), mimicking the cartilage surface, upon R-LUB injection were followed by a surface plasmon resonance spectroscopy and surface forces apparatus. The results indicated R-LUB can bind well on COL II surface and the layer of COL II/R-LUB complex exhibited a much lower nonspecific adsorption of BSA (3.25 ng/cm^2) and LYS (0.26 ng/cm^2) compared to those of the COL II layer (32.7 ng/cm^2, 7.26 ng/cm^2), respectively. Normal force measurement demonstrated there were repulsive forces between the COL II/R-LUB complex and different surfaces with $-COO^-$, $-NH_3^+$ and $-CH_3$ groups. Likewise, COL II had a high coefficient of friction ($\mu \sim 0.48$) with surface damage at 2 μm/s and wear pressure of 1.56 MPa. In contrast, the coefficient of friction of COL II/R-LUB complex was dramatically decreased to ~0.014-0.13 with surface damage at 13 μm/s, the complex even shows an ultralow coefficient of friction of 0.008 at the lowest loading <3 mN. Furthermore, R-LUB modification boosts the strength of the surface against abrasive wear (damage) of 11.96 MPa, which was 7.7 times higher than that of COL II alone. Hence, R-LUB may act as an anti-adhesive and lubrication layer adsorbed on COL II surfaces to develop strong steric-repulsive interactions and lubrication to prevent direct surface contact. Our results provide fundamental insights into the adsorption and lubrication behavior for understanding biological lubrication, especially using R-LUB for CACP disease treatment.

9:40am **BI+AS+PS-MoM-5 Hyaluronic Acid-Dopamine Conjugate for Facile Deposition onto Collagen I with Enhancing Anti-Adhesion and Lubrication***, H. Yuan,* Tianjin University, China*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria*; **Rongxin Su,*** Tianjin University, China

Collagen I matrix (COL I) has been applied clinically for repairing damaged cartilage, but it has poor protein resistance and insufficient lubrication performance, which seriously affects the repairing performance for cartilage. Hyaluronic acid (HA) has good anti-adhesive and lubrication properties, and seems to be a potential candidate to improve treatment with COL I, but it cannot be immobilized onto the collagen surface. Inspired by mussels, dopamine (DA) was chemically grafted to HA to form the HADA conjugate, which could firmly adhere to the surface of COL I by dopamine oxidation and reacted with amine from COL I. The protein resistance and lubrication properties of COL I and HADA-modified COL I (COL I/HADA) surfaces were followed by quartz crystal microbalance with dissipation and surface force apparatus techniques. The optimal modified time of HADA on COL I surface was 8 h. The nonspecific adsorption of bovine serum albumin (BSA) and lysozyme on COL I/HADA were reduced to 1/25 and 1/42 of that on COL I. COL/HADA also displayed very good resistant to high concentrations of BSA. Upon HADA modification, the interaction force between COL I and the surfaces with positive and negative charges sharply decreased from 2-6 mN/m to 0, demonstrating that the COL I/HADA surface had a strong anti-adhesion property. The coefficient of friction of COL I (~0.65) was quite high displaying poor lubricating ability, while that of COL I/HADA reduced to ~0.16. Upon HADA modification, the wear occurred at a shear rate of 14 μm/s, and the surface resistance to abrasive wear (damage) was greatly improved to 9.7 MPa, about 12 times higher than the COL I surface. These results indicated that HADA-modified COL I is a promising anti-adhesive and lubricating joint repair material, especially in the field of osteoarthritis treatment.

10:00am **BI+AS+PS-MoM-6 Anti-Fouling Properties of Amphiphilic Zwitterionic Hydrogels***, **Lisa Schardt,*** Ruhr University Bochum, Germany*; A. Martínez Guajardo,* University of Potsdam, Germany*; J. Koc,* Ruhr University Bochum, Germany*; J. Clarke, J. Finlay, A. Clare,* Newcastle University, UK*; H. Gardner, G. Swain, K. Hunsucker,* Florida Institute of Technology*; A. Laschewsky,* University of Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of organisms most likely due to their stable hydration shell.[1] Zwitterionic polymers like the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) are promising candidates foranti-fouling coatings. However, due to low mechanical strength, their performance in the field is limited.[2] N-butyl methacrylate (BMA) was added in amounts between 0 and 50% to copolymers containing SPE and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) to tune the hydrophilicity of the resulting hydrogel properties. The rearrangement of the polymer upon immersion in seawater was characterized by under-water contact angle goniometry. The swelling and resistance against mineral particles were measured with surface plasmon resonance (SPR) and sediment immersion tests. Biological anti-fouling experiments were performed using *Ulva linza* and field tests. Upon immersion in saltwater, the polymer chains rearranged to form hydrophilic surfaces and the degree of swelling depended on the salt concentration. The incorporation of BMA successfully altered the mechanical properties of the coatings resulting in a lower silt uptake. At the same time, the amphiphilicity did not hamper the anti-fouling performance in laboratory assays and a decrease of the settlement was observed in field tests.[3]

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10:40am **BI+AS+PS-MoM-8 Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion***, L. Mears, J. Appenroth, A. Celebi, A. Imre, H. Yuan,* TU Wien, Austria*; P. Bilotto,* CEST Centre for Electrochemistry and Surface Technology, Austria*; R. Su,* Tianjin University, China*; **Markus Valtiner,*** TU Wien, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. Here we critically discuss recent progress in the field, and we discuss how interfacial electrochemistry can vary interfacial forces by a concerted tuning of surface charging, hydration forces and tuning of the interfacial ion concentration. Mussel foot proteins contain a number of different functional groups, with much focus directed towards the catechol moiety. Therefore, we discuss some of our recent results in the area of adhesion of different functional groups in a saline environment. We also present new data from electrochemical surface force apparatus experiments that explore the difference in adhesion for oxidized and reduced forms of the catechol functional group against a mineral, mica, in different environments. These results raise interesting questions about the role of the catechol group. We propose new paths into understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

11:00am **BI+AS+PS-MoM-9 Bioinspired Underwater Adhesives Using Amyloids from Commonplace Proteins***, M. Wilson,* NRC Post-doctoral Fellow sited at the Naval Research Laboratory, Chemistry Division*; M. Beasley,* NRC post-doc sited at the Naval Research Laboratory, Chemistry division*; K. Fears,* Naval research laboratory, Chemistry Division*; E. Yates,* US Naval Academy, Chemistry Department*; **Christopher So**[1]*,* Naval Research Laboratory, Chemistry Division

Barnacles adhere permanently underwater using proteins that are delivered as a liquid, triggered to assemble, and cure as a bulk amyloid material in extreme seawater environments. More cosmopolitan than most other fouling organisms, barnacles rely on these materials to remain stuck at frigid ocean depths, as well as on hot intertidal coasts. We have previously been successful in designing sequences that can mimic the natural glue chemistry and structure, however bridging the gap between natural sequences and materials of practical use remains a challenge. Here, we mimic protein aggregation from the barnacle with unmodified food proteins as model systems and fabricate adhesives by curing them at the adhesive joint. We use temperature and time to control protein assembly and define the relationship between biophysical state and adhesive strength. Using thermal processing, we fabricate adhesives that approach the underwater lap shear strength of commercial marine and contemporary bioinspired chemistries. Though we observe differences in adhesive behavior between the examined proteins and their aggregation state, the presence of amyloids improves underwater performance across all proteins studied. We show that commonplace proteins can be delivered as a liquid, triggered to cure with chemistry or heat, and form strong underwater adhesives at the contact. The aggregation of commonplace proteins is therefore a viable pathway in creating strong underwater adhesives which, like the organisms that use them, can operate in extreme underwater conditions.

11:20am **BI+AS+PS-MoM-10 Incorporation of Antimicrobial Cyclic Peptides in Polymeric Materials***, D. Regan, Q. Lu, D. Barlow, **Kenan Fears,*** US Naval Research Laboratory

Polymeric coatings are used universally to protect structural materials and extend their operational lifetime. Microbial growth on these coatings, if unmitigated, present health risks and can diminish the protective performance of the coatings. For example, fungi have been linked to the

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[1] **BID Early Career Researchers Award**

degradation of aircraft surface coatings which can lead to corrosion of the underlying metals. After bans on heavy metal mixtures within surface treatments, a commercial void remains for a solution to prevent biodegradation of material surfaces. Building on the advancements within cyclic peptide synthesis, we test the antimicrobial activity of alpha and beta conformations of cyclic peptides against microorganisms of medical and industrial interest. Minimum inhibitory concentration (MIC) and microbial growth assays showed that cyclic peptides exhibited broad spectrum activity against gram-positive and gram-negative bacteria, yeasts, and algae. Furthermore, the cyclic peptides were mixed into a commercial polyester polyurethane coating, Irogran, and exposed to cultured isolates of biodegrading yeasts. For both cyclic peptide-Irogran blends, zero colony forming units were detected after a one-week exposure. These findings demonstrate how synthesized cyclic peptides retain their antimicrobial activity after incorporation into polymeric surface coatings to prevent the growth of problematic microorganisms.

11:40am **BI+AS+PS-MoM-11 Tuning Amphiphilicity of Alginic Acid-Based Polyelectrolyte Multilayers to Enhance Marine Fouling Resistance***, **Jana Karthäuser**, T. Gnanasampanthan, S. Spöllmann, R. Wanka, H. Becker, A. Rosenhahn,* Ruhr University Bochum, Germany

Polysaccharides are among other naturally occurring polymers commonly used in fouling-resistant coatings for both marine and medical applications. The anionic polysaccharide alginic acid (AA) is a non-toxic, eco-friendly, and readily accessible biopolymer that is widely used for biomedical purposes because of its high water-binding capacity. Thus, alginic acid is an interesting and promising building block to produce marine antifouling coatings. Unfortunately, in seawater, the biopolymer loses its antifouling efficacy due to the complexation of bivalent ions. An approach to overcome the susceptibility of charged polysaccharides, such as AA, is the blocking of the carboxylate groups by hydrophobic functional groups. The incorporation of amphiphilic moieties additionally changes the physicochemical properties of the coating and enables the tuning of fouling-resistant properties.[1]Layer-by-layer assembly of polyelectrolytes is a versatile and common technique to produce highly defined and reproducible coatings. The use of different or differently modified polyelectrolytes with opposite charges enables the charge-driven assembly.[2] To introduce amphiphilicity, different degrees of carboxyl groups of alginic acid were modified with pentafluoropropylamine. The influence of the amphiphilicity on the physicochemical characteristics of the modified alginic acid itself as well as of the coatings, when used alternately deposited with polyethyleneimine in multilayers, were investigated. Subsequently, the different degrees of modification of the AA-containing coatings with respect to the non-specific attachment of proteins by surface plasmon resonance spectroscopy and marine fouling organisms by attachment assays were examined in more detail and revealed an improved fouling resistance with increasing amphiphilicity.

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Gnanasampanthan, T. *et al.* Effect of Multilayer Termination on Nonspecific Protein Adsorption and Antifouling Activity of Alginate-Based Layer-by-Layer Coatings. *Langmuir***37**, 5950–5963 (2021).

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MEMS and NEMS Technical Group
Room 302 - Session MN+AS+NS+QS+SE-MoM

Dynamics and Engineering of MEMS/NEMS

Moderators: Jürgen Brugger, EPFL, Switzerland, **Eva Weig**, University of Munich, Germany

9:00am **MN+AS+NS+QS+SE-MoM-3 MEMS-Based Surface Nanoengineering Using Thermal AFM Probes: 30 Years and Counting***, **Jürgen Brugger**,* École Polytechnique Fédérale de Lausanne, Switzerland **INVITED**

Soon after the first publication in 1985 of the atomic force microscope (AFM) attempts were made to extend AFM-based surface probing from microscopy to lithography [reviewed in 1]. The potential applications in writing and reading for data storagein the early years served as technology driver and showed remarkable performances [2]. One of the variants of AFM-based writing (and reading) operates a heated nano-tip to perform thermally induced phase changes of materials. The three-fold combination of nano-scale heat localization (30 nm scale), high temperature (~ 500 °C)and particularly fast heating/cooling cycles (10E-6 s) is unique and opens new opportunities for surface engineering and material conversion using heat.In the meantime, nano-tips and cantilevers were further perfected as nanotools to locally induce phase changes in materials for a wide range of exploratory studies. Today, thermal scanning probe lithography (t-SPL) has matured into turn-key systems that can be compared to some extend to electron beam lithography, but without the useof charged particles and without the need for development. The full grasp of potential applications in R&D and production is still growing as the technique is still emerging.

In this talk, we will give first some background how heated AFM probes were initially designed and fabricated that led to today's advanced thermo-mechanical probe design of micro-cantilevers and nano-tips. The paper will then review some main achievements up to date [3] and then present recent results on t-SPL utilized for 2D materials by our own work [4, 5], and will conclude with some outlook on further challenges in hot-tip nanoengineering.

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10:40am **MN+AS+NS+QS+SE-MoM-8 Atomically-Thin MoS_2 Nanoelectromechanical Resonators***, R. Yang,* Shanghai Jiao Tong University, China*; **Jaesung Lee**,* University of Texas at El Paso **INVITED**

With the development of the Internet of Things (IoT), new sensors and signal processing elements that consume *near-zero* power to operate on resonance, have high tunability and small form factor are necessary.The ultralow mass and large resonance tunability make resonant 2D nanoelectromechanical systems (NEMS) suitable for ultrasensitive mass, force and biomolecular sensing, radio-frequency (RF) front end, and strain-tunable devices.Further, molybdenum disulfide (MoS_2) resonators only require picowatt level of power for sustaining the strong and stable resonance operations due to their ultralight weight.This opens an opportunity to explore new sensors and signal processing elements for IoT applications that really require near-zero power to operate on resonance, and at the same time, have wide dynamic ranges and tuning ranges. In this talk, we summarize our most recent advances in 2D MoS_2 NEMS resonators.

11:20am **MN+AS+NS+QS+SE-MoM-10 Can a Single Nanomechanical Mode Generate a Frequency Comb?***, **Eva Weig**,* Technical University of Munich, Germany **INVITED**

Doubly-clamped nanostring resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range. Dielectric transduction via electrically induced gradient fields provides an integrated control scheme while retaining the large mechanical quality factor [1]. Dielectrically controlled nanostrings are an ideal testbed to explore a variety of dynamical phenomena ranging from multimode coupling to coherent control [2]. Here I will focus on the nonlinear dynamics of a single, resonantly driven mode. The broken time reversal symmetry gives rise to the squeezing of the string's fluctuations. As a result of the high mechanical Q factor, the squeezing ratio is directly accessible from a spectral measurement [3]. It is encoded in the intensities of the two spectral peaks arising from the slow dynamics of the system in the rotating frame. For stronger driving, an onset of self-sustained oscillation is observed which leads to the generation of a nanomechanical frequency comb. The effect is a consequence of a resonantly induced negative effective friction force induced by the drive. This is the first observation of a frequency comb arising solely from a single mode and a single, resonant drive tone [4].

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Nanoscale Science and Technology Division
Room 304 - Session NS2+AS+EM+SS-MoM

Quantum Based Sensors and Metrology

Moderator: Nikolai Klimov, National Institute of Standards and Technology

10:40am **NS2+AS+EM+SS-MoM-8 Interfacing Biomolecules with Coherent Quantum Sensors*, Peter Maurer,*** University of Chicago **INVITED**

Quantum optics has had a profound impact on precision measurements, and recently enabled probing various physical quantities, such as magnetic fields and temperature, with nanoscale spatial resolution. In my talk, I will discuss the development and application of novel quantum metrological techniques that enable the study of biological systems in a new regime. I will start with a general introduction to quantum sensing and its applications to nanoscale nuclear magnetic resonance (NMR) spectroscopy. In this context, I will discuss how we can utilize tools from single-molecule biophysics to interface a coherent quantum sensor with individual intact biomolecules, and how this could eventually pave the way towards a new generation of biophysical and diagnostic devices.

Surface Science Division
Room 319 - Session SS+AS+TF-MoM

Dynamics and Mechanisms at Surfaces and Interfaces

Moderator: Eric Altman, Yale University

8:20am **SS+AS+TF-MoM-1 Stereodynamics Effects in Grazing-Incidence Fast-Molecule Diffraction***, **Cristina Díaz,*** Universidad Complutense de Madrid, Spain **INVITED**

Grazing-incidence fast-projectile diffraction, measured experimentally for the first time in 2007[1,2], has been proposed both as a complement and an alternative to thermal-energy projectile scattering, which explains the interest that this technique has received in recent years, especially in the case of atomic projectiles (GIFAD)[3,4]. Grazing-incidence fact-molecule diffraction (GIFMD), on the other hand, has received much less attention (mostly theoretical[5,6]), despite the fact that the H_2 molecule:(i) is as easy to generate as atomic H (a widely used projectilein GIFAD experiments); (ii) is lighter than He (another widelyused projectile in GIFAD), which would further reduce surface-phononsinelastic processes; and (iii) can reveal aspects of thesurface landscape that may be relevant in other contexts dueto the internal degrees of freedom (DOFs) and, in the case ofthe ionic surfaces, to the interaction of its quadrupole momentwith the electric field created by the ionic crystal, which is verysensitive to the surface details.Here, we present a theoretical study of grazing-incidence fast-molecule diffraction of H_2 from KCl(001) usinga six-dimensional density functional theory based potential energy surface and a time-dependentwavepacket propagation method. The analysis of the computed diffraction patterns as a function ofthe molecular alignment, and their comparison with the available experimental data, where the initialdistribution of rotational states in the molecule is not known, reveals a puzzling stereo dynamics effectof the diffracted projectiles: Diffracted molecules aligned perpendicular, or quasi perpendicular,to the surface reproduce rather well the experimental diffraction pattern, whereas those moleculealigned parallel to or titled with respect to the surface do not behave as in the experiments. Theseresults call for more detailed investigations of the molecular beam generation process.

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9:00am **SS+AS+TF-MoM-3 Intermolecular Interactions in Carbonyl Compounds Trigger Surface Reactivity***, **Swetlana Schauermann**, S. Attia, C. Schroeder, M. Schmidt,* Kiel University, Germany

Hydrogenation of carbonyl compounds is an important step in many applications in heterogeneous catalysis. This class of reactions is, however, experimentally highly challenging as it requires the activation of a normally very stable C=O bond. There is an ongoing discussion on an alternative mechanism of C=O bond hydrogenation, which involves keto-enol tautomerization as a first step. In this mechanism, a H atom transfers to oxygen in an intramolecular process to produce a C-O(H) single bond, leaving behind a C=C double bond and forming the enol species. Several theoretical studies predict a significantly lower activation barrier for hydrogenation of the C=C bond in enol as compared to the direct hydrogenation of the C=O bond in ketone for different classes of mono- and dicarbonyl compounds.

In this contribution, we present a mechanistic study on atomistic-level mechanisms of enol formation and stabilization via lateral interactions with co-adsorbed surface species over catalytically active metal surfaces (Pt and Pd).[1, 2] We employ a broad range of carbonyl compounds including acetophenone, acetylpyridine, butanal and ethyl pyruvate, whose adsorption and reactivity behavior were investigated using a combination of infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM) and molecular beam techniques. We found that enols can be efficiently formed in different types of carbonyl-containing molecules, however, they require stabilization on the surface via lateral interaction, e.g. by establishing hydrogen bonding between the –OH group of an enol and a carbonyl group of the neighboring adsorbate. Stabilization of formed enols via lateral interactions with the adjustment molecules results in formation of different types of oligomers, including one of more enol molecules. The efficiency of enol formation was found to strongly depend on the chemical structure of the adsorbates and can be affected by e.g. the insertion of the functional groups, such as phenyl or pyridine groups. Also the presence of subsurface hydrogen in Pd was shown to strongly enhance keto-enol tautomerisation in some of the investigated carbonyls. Finally, we provide the first experimental evidence for a low-temperature hydrogenation pathway of carbonyl compounds, which occurs in ketone-enol dimers of acetophenone formed on Pt.[3] In this process, stabilization of enol species via lateral interactions with a neighboring carbonyl is crucial for enabling the target hydrogenation pathway.

1. Attia, S. et al *Angew. Chem. Int. Edit.* **2018,***57*, 16659.
2. Attia, S.et al *ACS Catal.* **2019,***9*, 6882.
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9:20am **SS+AS+TF-MoM-4 Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)**, ***Arved Cedric Dorst**, T. Schäfer,* University of Göettingen, Germany*; D. Killelea,* Loyola University Chicago

In heterogeneous catalysis, the reactivity of for example oxidation reactions is often enhanced by transition group metal surfaces as catalysts. After exposure, the oxygen molecules readily dissociate into oxygen atoms on the surface forming characteristic surface reconstruction patterns. However, not only the formation of surface oxygen (O_{surf}) structures but also of subsurface oxygen (O_{sub}) phases is possible, especially when aggressive oxidation agents such as NO_2 or atomic oxygen are used as oxygen source. The O/Rh(111) has been adapted as a benchmark system for O_{sub} formation in the past. In temperature programmed desorption (TPD) experiments, O_{sub} emerges as a narrow desorption feature around 800 K, while O_{surf} forms a subsequent broad desorption feature over several 100 K. Although extensive research has been done on the formed reconstructions of O_{surf}, few is known about the microscopic details of O_{sub} formation.

In the here presented work, velocity map imaging (VMI) was applied to the O/Rh(111) system. We combined TPD and VMI to investigate recombinatively desorbing O_{sub} from Rh(111). This allows a precise assignment of high-resolution velocity distributions of desorption products to certain TPD peaks. We observe a hyperthermal velocity distribution for recombinatively desorbing oxygen from subsurface as well as from surface states. These results provide valuable benchmark data, on which theoretical models describing subsurface oxygen dynamics can be developed and tested.

9:40am **SS+AS+TF-MoM-5 In-Situ Characterization of O_2 Gas-Induced Rearrangement of Near-Surface Composition in Refractory High-Entropy Alloys***, H. Kersell,* Oregon State University*; X. Fan,* University of Tennessee Knoxville*; A. Herman,* Oregon State University*; Z. Lyu,* University of Tennessee Knoxville*; B. Steingrimsson,* Imagars LLC*; P. Liaw,* University of Tennessee Knoxville*; **Gregory S. Herman**,* Oregon State University

Alloy formation enables the enhancement of material properties from electrical and thermal conductivity, to magnetism, chemical reactivity, and mechanical strength and ductility. For example, Ti alloys are lightweight, corrosion resistant, have low Young's modulus, and possess tunable strength and ductility at high temperatures. Their corrosion resistance and low Young's modulus make them suitable for biomedical implants, while their light weight, tunable strength, and high working temperatures facilitate use in high-temperature applications. Traditional alloys often contain a principal metal comprising most of the alloy composition, with additional functionality (e.g., oxidation resistance) induced by minority components. In contrast, high-entropy alloys possess multiple principal components, and have recently attracted significant attention for their enhanced tunability and sometimes unexpected physical properties.

Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we have probed the initial oxidation of $TiZrHfNb_{0.3}$ refractory high-entropy alloys (RHEAs). Sputter-cleaning the as-cast alloy in ultrahigh vacuum removes adventitious carbon and native oxides, revealing a metallic alloy containing metal carbide species through its bulk. Subsequent vacuum annealing from room temperature (RT) to 100° C enriches the near-surface carbide content. This near-surface carbide enrichment continues with increasing temperature, accompanied by the formation of surface hydrocarbon species. Meanwhile, the relative compositions of Ti, Zr, Hf, and Nb are stable across the same temperature regime in vacuum. Despite their thermal stability, freshly sputter-cleaned, metallic alloy surfaces exposed to 1 mTorr of O_2 gas become enriched by a near-surface layer of Hf- and Zr- oxides. At the same time, the carbide component is suppressed, and a metal-oxide interface, containing Ti- and Zr- oxides, appears within the XPS probing depth (~8 nm). Subsequent RT oxygen exposure at higher O_2gas pressures induces comparatively minor changes in the surface oxide layer composition.

These results reveal the formation and nature of a thin protective oxide layer at the $TiZrHfNb_{0.3}$ RHEA surface in response to mild oxygen pressures. We present these results in terms of the O_2 pressure/temperature parameter space and discuss implications for the $TiZrHfNb_{0.3}$ RHEA behavior.

10:00am **SS+AS+TF-MoM-6 Surface Faceting and Oxidation in Binary and Ternary Ni-Based Alloys***, **Devin Jessup**, K. Orson, Z. Harris, P. Reinke,* University of Virginia

Future-proofing materials against degradation and failure means designing alloy systems with corrosion resistance built-in, and this is especially important for alloys in extreme environments. Ni-based superalloys are alloyed with Cr, Mo, and W which help form protective layers that are highly corrosion resistant mostly due to chromia (Cr2O3) formation. On polycrystalline alloy surfaces a wide range of crystallographic orientations coexist and are defined by the individual grains. For these often highly stepped or kinked surfaces, a complex surface faceting results from the tendency to minimize the surface free energy leading to an alloy with variable and complex surface topographies. Prior research indicates that different oxide species will nucleate along specific orientations resulting in oxide layer heterogeneity, which can introduce points of failure in the protective layer. Our work focuses on how these differences in surface crystallographic orientation can result in changes in the nucleation and growth of NiO and chromia, whose growth is kinetically controlled under our oxidation conditions.

A Ni11wt%Cr6wt%Mo alloy sample with large grains up to 1 mm offering a wide array of crystallographic orientations was selected for characterization. Scanning Tunnelling Microscopy (STM), Electron Backscatter Diffraction (EBSD), and Scanning Electron Microscopy (SEM) are used to characterize the surface. The native oxide was removed by annealing to 640˚C, and the highly variable surface topography was studied over a range of grains catalogued by EBSD. The alloy shows several unique surface topographies which are controlled by crystallographic orientation. Several examples are included in the supplemental material, which include wave-like facet structures, sharply terminating saw-tooth facets, and flatter “matchstick” structures. These can be correlated with the Miller index of the underlying grain surface on the stereographic triangle. The surface morphology was quantified with respect to facet size, shape, heights, orientation, and spatial distribution. This analysis provided the Miller indices for all well-expressed facets. Grain orientations were matched with their surface structures through a combination of feature matching between SEM and STM imagery and Fast Fourier Transform analysis. Further work will observe oxide nucleation on these facets, and their impact on oxide formation and performance. Understanding these mechanisms will contribute to our understanding of how to design Ni-based alloys for the most stable protective layer.

10:40am **SS+AS+TF-MoM-8 Medard W. Welch Award Talk: Atomistic Simulations to Advance Surface Science***, **Susan Sinnott**[1],* Pennsylvania State University **INVITED**

Computational methods are useful tools in the investigation of atomic and molecular dynamics and associated mechanisms at surfaces and interfaces. Physics-based classical potentials are a class of computational method that is useful for use in classical atomistic simulations of systems made up of thousands to many billions of atoms. These potentials consist of parameterized functions that capture aspects of atomic and molecular interactions within these material systems.

The focus of this presentation is on the third-generation charge-optimized many body (COMB3) potential. COMB3 was developed to enable an atomic-scale description of systems that include combinations of metallic, ionic, and covalent bonding under the same framework. The framework enables the system to determine the charge state of an atom or ion and manifest the physically appropriate type(s) and strength of local bonding as a function of environment correctly and autonomously. The framework further includes a combination of atomic-specific, bond-specific, bond-angle-specific parameters; the former is the same regardless of material, and only new bond-specific and bond-angle-specific parameters are required to extend existing elements to new compounds.

This presentation will provide an overview of the COMB3 potential and illustrate its utility in the study of water-metal surface and nanoparticle interactions, the examination of carbon nanoparticle-metal surface interactions, and the mechanisms associated with the growth of metal films on metallic and oxide substrates.

11:20am **SS+AS+TF-MoM-10 STM Study of Ag Encapsulation of Pd and Pt Islands on Ag(111) at Room Temperature***, **Buddhika Alupothe Gedara**[2], M. Trenary,* University of Illinois - Chicago

PdAg and PtAg bimetallic catalysts are used in many important industrial applications. Therefore, an atomic scale understanding of these catalysts is important for their further development. In this study, the initial stages of submonolayer growth of Pd and Pt islands on Ag(111) at room temperature were investigated using scanning tunneling microscopy (STM). Although Pd (1.7 J m^{-2}) and Pt (2.2 J m^{-2}) have higher surface free energies than Ag (1.1 J m^{-2}) and a similar lattice mismatch (PdAg = 4.8% and PtAg = 4.2%), Pd and Pt show different behavior after deposition on Ag(111) at room temperature. Hexagonal Pd islands are formed on Ag(111) regardless of the coverage. In contrast, Pt shows a high density of small clusters and larger islands indicating less mobility for Pt than Pd on Ag(111). Due to Pd atom place exchange with Ag atoms, Pd-rich brims were observed at the ascending Ag step edges. But, Pt-rich brims were not observed. Because of the absence of Pt-rich brims , removal of Ag atoms created bays at the step edges. Surface Ag atoms migrate to cover both Pd and Pt islands, even at room temperature, creating vacancy pits on the Ag(111) surface. In addition to large vacancy pits, small mobile vacancy pits were observed on Pt/Ag(111). Pd and Pt islands show different moire structures on Ag(111) even though they have almost same lattice mismatch. Migrated Ag atoms nucleate near the center of Pd islands to grow the second layer, whereas, migrated Ag atoms nucleate at the corner of the Pt islands.

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[1] **Medard W. Welch Award Winner**

[2] **SSD Morton S. Traum Award Finalist**

2D Materials Technical Group
Room 303 - Session 2D+AS+SS-MoA

2D Materials: Defects, Dopants, Edges, Functionalization, and Intercalation

Moderators: Chih-Kang (Ken) Shih, University of Texas at Austin, **Young-Woo Son**, Korea Institute for Advanced Study, Republic of Korea

2:20pm **2D+AS+SS-MoA-3 Effect of Defects in 2D Materials on the Dielectric Breakdown***, **Abdulrahman H. Basher**, M. Lanza, U. Schwingenschlogl,* King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Two-dimensional (2D) materials are one of today's hot topics in the semiconductor industry due to the fact that they can be used to fabricate nanodevices with attractive properties [1, 2]. However, they may lose their features in the presence of defects. For instance, 2D hexagonal boron nitride (hBN) is an excellent insulator but defects lower its breakdown voltage in the experiment [3]. Therefore, the aim of this study is to understand the mechanism of the dielectric breakdown in hBN as compared to amorphous boron nitride (aBN), using first-principles calculations based on density functional theory. The CP2K quantum chemistry and solid-state physics software package is used (quickstep algorithm based on the Gaussian and plane waves method) [4, 5]. The generalized gradient approximation of Perdew-Burke-Ernzerhof [6] is employed, and Grimme's dispersion correction [7, 8] with Becke-Johnson damping [9] is used as the van der Waals forces play a significant role in 2D materials. The obtained densities of states show that the size of the band gap decreases for increasing defect density, confirming that 2D materials are sensitive to defects. We explain the experimental observation that the breakdown voltage decreases from hBN (crystalline) to aBN (amorphous).

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2:40pm **2D+AS+SS-MoA-4 Palladium Nucleation and Alloying at the WTe_2(001) Surface***, **Prescott E. Evans**, P. Sushko, Z. Dohnálek,* Physical and Computational Sciences Directorate and Institute for Interfacial Catalysis, Pacific Northwest National Laboratory

A deeper understanding of atomic-scale functionalization of transition metal dichalcogenides, especially topologically interesting variants such as WTe_2, is critical in developing deployable structures in quantum information science. Discerning the role of intrinsic surface defects as adsorption and functionalization sites is a key step towards device realization. In this study, scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and density functional theory (DFT) were utilized to examine the initial nucleation and growth of palladium on the WTe_2(001) surface as both a function of coverage and temperature. XPS measurements of the WTe_2(001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of $PdTe_2$ in electronic structure with an absence of interaction between Pd and tungsten. Using STM, we found palladium deposited at room temperature, where Pd clusters outnumber surface defects more than 10:1, produced no change in surface defect density. This indicates a lack of interactions between deposited Pd clusters with intrinsic surface defects. The annealing temperature-dependent STM studies further show that palladium clusters are stable to about 475 K. Palladium deposition at an elevated temperature of 425 K was performed to determine that the lack of nucleation on defects is, in fact, not a result of diffusion limitations during the growth. Complementary theoretical studies predict that palladium atoms interact strongly with Te adatoms and Te vacancies, while only binding weakly on pristine WTe_2(001). Based on these results, we conclude that the nucleation of Pd clusters is initiated by mobile Te adatoms that likely significantly outnumber other surface defects. Our high-temperature Pd deposition studies further support this assertion. Atomically resolved images of large Pd nanoparticles annealed above 475 K exhibit a superstructure on the top terrace indicating alloying with tellurium. Atomically precise, tailored heterostructures with tunable electronic, and topological properties are necessary for the growing need for quantum devices. A full account of the surfaces of these quantum materials, as in with WTe_2(001) where excess chalcogenide complicate interactions at the surface, is vital in directing both accurate predictive theory and material synthesis efforts.

3:00pm **2D+AS+SS-MoA-5 Advanced Doping Schemes for 2D Nb:WS_2 for Catalysis and Electronics***, **Jeff Schulpen**, C. Lam, W. Kessels, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor

Two-dimensional semiconductors such as WS_2 are promising materials for use in next-generation nanoelectronics due to their high mobility and scalability allowing for ultra-short gates. Doping is required to make the p-type FETs needed for CMOS logic and doping can also reduce the contact resistance, which is another important challenge to overcome for transistors based on 2D materials.[1] Separately, doped 2D materials are receiving interest as affordable catalysts, as the dopants enhance the catalytic activity of the basal plane in addition to the already high activity of the edge sites.[2]

Essential for both electronic and catalytic applications is the precise control over the amount and distribution of dopants in the film. The synthesis method of atomic layer deposition (ALD) allows excellent control over these parameters such that e.g. graded doping profiles and edge decorations can be achieved.[3]

In this work we synthesize Nb-doped WS_2 by plasma-ALD and characterize the electronic and catalytic performance of the films.Conventional supercycles of type $(AC)_m(BC)_n$ were used to achieve excellent composition control from W-rich to Nb-rich films. Optimal hydrogen evolution reaction (HER) activity was found for Nb-rich films (~85% Nb). Beyond composition tuning, we investigate the effect of different edge terminations on the HER activity by modifying the cycle order in the ALD process. For electronic applications where low dopant concentrations are relevant, we use a modified $(AC)_m(ABC)_n$ scheme, where adsorbed W precursor largely inhibits adsorption of the Nb precursor. This allows for better dopant distribution than conventional supercycles, thereby improving the resistivity and Hall mobility of the films by a factor of two. Further characterization of devices based on the grown films is presented.

These results confirm that ALD-grown Nb-doped WS_2 is a promising material for both electronics and catalysis, and that the use of advanced doping schemes can further improve the performance of these films. This also serves as a demonstration of inhibition-assisted doping using ALD, which could be of interest for other material systems.

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3. Schulpen, J. J. P. M. *et al. 2D Mater.***9**, 025016 (2022).

4:00pm **2D+AS+SS-MoA-8 Atomic Imaging of Dynamic Behaviour at 2D Material Solid-Solid and Solid-Liquid Interfaces***, **Sarah Haigh**,* University of Manchester, UK **INVITED**

Transmission electron microscopy (TEM) is used for understanding the local structure of nanomaterials. Although, we are frequently concerned about understanding behaviour during chemical reactions or while undergoing physical processes, most TEM is performed with the sample exposed to high vacuum, which can change the atomic structure of surfaces and interfaces. Unfortunately, commercial in-situ liquid, gas or electrochemical cell TEM imaging holders often severely limit atomic resolution imaging and chemical analysis.

For investigating the chemical reactivity and degradation of 2D materials without exposing them to the TEM vacuum, an effective approach is to encapsulate the sample between two inert and impermeable few-layer 2D sheets (such as graphene or hexagonal boron nitride). This also enables transfer of air sensitive specimens from an inert vacuum or glove environment to the TEM without exposing the material to atmospheric conditions. We have applied this approach to study air sensitive 2D materials, including local point defects, doping and edge structures in a wide range of structures (e.g. CrBr3, GaSe, black phosphorus) (Fig. 1c)[1,2]. We also find that encapsulation with inert 2D materials is an effective route to preserve the delicate surface structure of hydrated 2D materials, enabling the visualization of exchangeable surface cations on few layer clays and micas [3] and a route to understand the changes in atom/ion motion at interfaces where the 2D materials are twisted with respect to each other (Fig. 1d).[3,4]

This 2D heterostructure approach can also be used to investigate solid-liquid interfaces. Building on nanochannel technology developed by the group of Andre Geim (Fig. 1b)[5] we have developed in-situ liquid phase TEM imaging using 2D heterostructure nanochannels. The in-situ 2D heterostructure liquid cell approach provides atomic resolution imaging and analysis and makes it possible to study the earliest stage of chemical synthesis [6]. It also reveals the large differences in adatom adsorption sites on 2D surfaces in vacuum compared to hydrated environments and allows study of dynamic adatom motion at solid liquid interfaces [7]; something that was not previously possible by any technique (Fig. 1a).

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4:40pm **2D+AS+SS-MoA-10 Electrodeposition of Nanofiberous H-Type MnO_2 Birnessite on Epitaxial Graphene Silicon Carbide Heterostructures, and transformation to Alkali Birnessites (Na, Li, K) via Simple Intercalation***, **Michael Pedowitz**, D. Lewis, K. Daniels,* University of Maryland, College Park

Mixed valence manganese oxides (MnO_x) have attracted significant research interest in recent years due to the reversible low energy redox reactions between manganese oxidation states (Mn^{+2}, Mn^{+3}, and Mn^{+4})[1], which has enabled its use in catalysis[2], energy storage[3], and gas sensing[4]. Of these manganese oxide compounds, manganese dioxide (MnO_2) has been of particular interest due to its wide variety of synthesized structural polymorphs (α (1x2 tunnel), β (1x1 tunnel), γ (spinel), and δ (layered))[5] which allow for significant control over the active surface area and reactive properties MnO_2. In particular, the Mn^{+3} defect density, which has been found to increase the reactivity of the MnO_2 film[6], is highly variable between polymorphs, with the δ phase exhibiting the highest defect density. Water stabilized δ-MnO_2 (H-δ-MnO_2) in particular contains the highest number of Mn^{+3} defects due to the presence of $Mn^{+2/+3}$ in the interlayer, which neutralize the layer charge from lattice defects[7]. However, the production of H-δ-MnO_2 has proven challenging in the literature. In this work, we present the synthesis of H-δ-MnO_2 on epitaxial graphene silicon carbide via electrodeposition. The electrodeposition was carried out in a 3 electrode electrochemical cell in a 3-step process with a duration of 1.25 seconds. The resulting films were then characterized using a combination of Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) to confirm the formation of H-δ-MnO_2 and probe its surface morphology. The Raman spectra indicated the successful formation of H-δ-MnO_2, while the AFM and SEM indicated the surface has a nanofibrous character, increases the active surface area of the thin film. We then demonstrated that the material can be converted to Alkali type (Li, Na, K) δ-MnO_2 via intercalation without damaging the EG substrate. After the process, the material was characterized again with Raman, AFM, and SEM, which confirmed the transformation from H-type to Alkali-Type. As the interlayer spacing of δ-MnO_2 and its applications are related to the intercalated ions, this demonstrates the tunability of this heterostructure and its potential to be a platform for a variety of applications, including energy storage and gas sensing.

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5:00pm **2D+AS+SS-MoA-11 Signature of Coexistence of Ferroelectricity and Ferromagnetism in a Quantum Material***, **I-Hsuan Kao**, S. Yuan, J. Katoch, S. Singh,* Carnegie Mellon University

Electric field-controlled magnetism by combining van der Waals (vdW) based semiconducting ferromagnets and Weyl semimetal is appealing because of the gate tunability and efficient charge-spin transduction[1], which can be exploited for modular memory and logic devices. Ferroelectric switching has been previously demonstrated in bilayer and trilayer WTe_2[2-4], where the polarity can be controlled by electric gating. VdW based semiconducting FMs, such as $Cr_2Ge_2Te_6$ (CGT), provide the opportunity to study tunable magnetic phenomena and to build superlattices with other quantum materials[5]. By coupling a semiconducting ferromagnet to a Weyl semimetal, magnetization can be induced at the interface by magnetic proximity effect. We have fabricated WTe_2/CGT devices and observed anomalous Hall effect, which is a signature of magnetic proximity effect. In the same device, we are able to perform ferroelectric switching of WTe_2 by applying an electric field. Furthermore, the presence of the anomalous Hall effect can be enhanced (suppressed) by negative (positive) electric gating. We will present detailed measurements, which are required to understand this novel platform where ferroelectricity and ferromagnetism coexist.

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Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EL+MS+SS-MoA

Advancing Metrology and Characterization to Enable Atomic Scale Processing

Moderators: Steven M. George, University of Colorado at Boulder, **Rudy Wojteki**, IBM Almaden Research Center

1:40pm **AP+AS+EL+MS+SS-MoA-1 Nanoscale Chemical Analysis and Mapping of Atomic and Molecular Scale Processes via Infrared Photo-Induced Force Microscopy***, **Sung Park**,* Molecular Vista **INVITED**

As semiconductor device feature sizes move beyond the sub-7 nm technology node, atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) are being adopted to gain control over key processing parameters.These techniques are commonly combined with thin polymer barrier layers such as self-assembled monolayers (SAM) that are selectively located to achieve area selective deposition or etching. In protein and DNA chips, monolayers of specific molecules are engineered and patterned to guide the target molecules to specific locations.Common to these devices and processes are the atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials which demand new metrology and characterization techniques to assess and monitor these advanced processing techniques.Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-5 nm spatial resolution).The spectroscopic capability is useful for ascertaining the presence and quality of the molecular species. The mapping capability is useful for investigating surface functionalization and chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, sequential infiltration synthesis, and a variety of area-selective deposition techniques. PiFM applications on various atomic and molecular scale processes will be presented.

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2:20pm **AP+AS+EL+MS+SS-MoA-3 Area-Selective Deposition/Patterning of Boron Carbide Layers: Etch Studies***, **Raja Sekhar Bale**, R. Thapa, A. Caruso,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* University of Missouri-Kansas City

The semiconductor industry is pushing the boundaries of device scaling by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, silicon-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to its compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area-selective atomic layer deposition (AS-ALD) strategies. Herein we explore schemes for the selective dielectric on metal/dielectric deposition of boron carbide using monolayer and layer-by-layer methods. In particular, we focus on etch studies (wet and dry) toward understanding the stability and removal of these layers. X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques are employed for the characterization and imaging of the resulting surfaces.

2:40pm **AP+AS+EL+MS+SS-MoA-4 Smoothing of Surfaces by Atomic Layer Deposition and Etching***, S. Gerritsen, N. Chittock, V. Vandalon, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; E. Kessels,* ***Adrie Mackus,*** Eindhoven University of Technology, The Netherlands

With critical dimensions scaled down to the nanoscale in current electronics, surface and interface roughness increasingly limit device performance. In this work, we use simulations and experiments to explore whether atomic layer deposition (ALD), atomic layer etching (ALE) and combinations of these techniques can be used to smoothen surfaces, while processing materials with excellent uniformity and atomic scale control. The smoothing is experimentally demonstrated by atomic force microscopy and transmission electron microscopy analysis.

Many previous studies have shown that ALD and ALE can smoothen surfaces,[1,2] but the extent of smoothing has not been systematically characterized and the mechanisms of smoothing are only partly understood. In our studies, finite difference simulations were performed that describe ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point. Al_2O_3 ALD experiments using TMA and O_2 plasma validated this uniform front propagation model. A smoothing rate of $5.5\cdot10^{-3}$ nm RMS roughness reduction per nm of deposition was determined, revealing that significant smoothing by ALD requires relatively thick films (e.g. > 20 nm).

Al_2O_3 ALE from TMA and SF_6 plasma[3] resulted in a larger roughness reduction of $9.8\cdot10^{-3}$ nm/nm, which is explained by considering that the fluorination of the surface depends on the local curvature, such that peaks are smoothed more than valleys. In other words, for ALE two mechanisms contribute to the smoothing, i.e. uniform front propagation and curvature-dependent fluorination. In order to benefit from the enhanced smoothing by ALE, especially combinations of ALD and ALE in supercycle recipes can be very effective in smoothing surfaces, as will be highlighted in the contribution.

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3:00pm **AP+AS+EL+MS+SS-MoA-5 Thermal Atomic Layer Etching of Amorphous Aluminum Nitride Using Sf$_6$ Plasma and Al(Ch$_3$)$_3$***,* ***Haozhe Wang****, A. Houssain, D. Catherall, A. Minnich,* California Institute of Technology

We report the thermal atomic layer etching (ALE) of amorphous aluminum nitride using sequential exposures of low-power SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 ˚C, with etch rates varying with temperature from 0.1 Å/cycle at 200 ˚C to 1.9 Å/cycle at 300 ˚C, as measured using ex-situ ellipsometry. The self-limiting nature of the reactions was established by verifying that no etching occurred with only SF_6 or TMA. The etched surface was characterized using atomic force microscopy and x-ray photoemission spectroscopy. After 50 cycles of ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a∼35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and semiconductor devices.

3:20pm **AP+AS+EL+MS+SS-MoA-6 Thermal Atomic Layer Etching using MoF6-H2O precursors***,* ***Anil Mane,*** *J. Elam,* Argonne National Laboratory, USA

Well controlled atomic layer etching (ALE) processing is needed for the creation of next generation complex 3D devices. A simple semiconductor processing compatible thermal ALE method is preferred for the process integration point of view. Recently we have developed the MoF6-H2O precursors based etching methods for the etching of atomic layer deposited (ALD) TiO2, Ta2O5 and MoS2 in a precise controlled manner. The etch rate and etch behavior of these materials mainly controlled by processing temperature (100-325^{o}C) and precursors dose times. The MoF6-H2O etching process of these ALD grown TiO2, Ta2O5 and MoS2 was studied by in-situ methods such as infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), and spectroscopic ellipsometry (SE). Additionally, at present we have also developed novel in-situ calorimetry method to measure chemical reaction heat in ALE precursor's reaction. Here some of latest results on this in-situ ALE-calorimetry method will also be presented.

4:00pm **AP+AS+EL+MS+SS-MoA-8 The Thinner, the Better - Characterization of Ultra-Thin Films by Low Energy Ion Scattering (Leis)***,* ***Thomas Grehl,*** IONTOF GmbH, Germany **INVITED**

Current and future thin film processes require quantitative characterization from the early phases of film growth to complex film stacks with a total thickness of only a few nm. While many surface analytical techniques are challenged by this requirement, Low Energy Ion Scattering (LEIS) analysis is ideally suited for ultra-thin film and sub-monolayer characterization. The key property is its single atomic layer information depth.

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring of the surface composition.

In addition to the surface composition, also the distribution of elements over the first few nm of the sample is contained in the spectra. The so-called "in-depth information" is acquired in a virtually non-destructive way, avoiding sputtering and therefore the long measurement times and artefacts associated with it. For sufficiently thin films, the depth resolution is only a few Å. This allows to study the development of the film thickness while also monitoring film closure to determine the growth mode.

In some cases, low energy noble gas sputtering is applied to extend the depth range beyond a few nm or to handle complex materials where "in-depth" and surface information cannot be deconvoluted.

In this contribution, we will highlight a number of examples from quite different materials and film systems. These will be used to illustrate how LEIS is applied in practical way. We will show how LEIS contributes unique information for modern ultra-thin film characterization.

4:40pm **AP+AS+EL+MS+SS-MoA-10 Intrinsic Area Selective Atomic Layer Deposition of MoS$_2$ Thin Films***, J. Soares,* ***Wesley Jen****, S. Hues,* Boise State University*; J. Wensel,* Micron Technology Inc*; E. Graugnard,* Boise State University

As the critical dimensions in today's semiconductor devices continues to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of S = 0.94 after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

5:00pm **AP+AS+EL+MS+SS-MoA-11 In Situ Measurements of Surface and Film Stress during Atomic Layer Deposition of Al_2O_3 and AlF_3 using Wafer Curvature Techniques***, **Ryan B. Vanfleet**, E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The in situ measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress then decreases with increasing deposition temperature. These in situ temperature-dependent Al_2O_3 ALD film stresses are in good agreement with ex situ film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These in situ measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional in situ measurements have explored the surface and film stresses during AlF_3 ALD using TMA and HF as the reactants. AlF_3 ALD showed similar surface stress behavior to Al_2O_3 ALD. The TMA exposure again results in a compressive stress attributed to repulsion between surface methyl groups. The HF exposure then removes the methyl groups and releases the compressive stress. At AlF_3 ALD temperatures between 150-200°C, the compressive surface stress resulting from the TMA exposures is ~0.45 N/m. In marked contrast to Al_2O_3 ALD, AlF_3 ALD displayed no film stress during film growth. This lack of film stress in AlF_3 ALD films may be related to the nature of the AlF_3 ALD film as a molecular solid.

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Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA
Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES***, **David Cant**,* National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES***, **Thierry Conard**, A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as $TiN/HfO_2/SiO_2/Si$ as well as more complex stacks such as $TaN/TiAl/TiN/HfO_2/SiO_2/Si$ or $W/TiN/HfO_2/SiO_2/Si$. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

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[1]https://www.ulvac-phi.com/en/products/xps/quantes/

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2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich, **Andreas Thissen**,* SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*;* ***Christopher Moffitt,*** Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the "tool". In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable – delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***,* ***Alberto Herrera-Gomez,*** *D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

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[2] D.-M. Guzman-Bucio, A. Carmona-Carmona, M.A. Gonzalez-Reyna, A. Herrera-Gomez, Peak and background parameters of the 3d core level of the pure second row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[3] A. Herrera-Gomez, D. Cabrera-German, A.D.A.D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, L. Gomez-Muñoz, L.G.M. Herrera-Gomez, Alberto., Dagoberto Cabrera-German., Anthony D. Dutoi., Milton Vazquez Lepe., Servando Aguirre-Tostado., Piero Pianetta., Dennis Nordlund., Orlando Cortazar-Martinez., Alejandro Torres-Ochoa., Oscar Ceballos-Sanchez., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. https://doi.org/10.1002/sia.6364.

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4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***,* ***Lev Gelb****, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first 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. The only required inputs to the calculation are the "fractional composition" profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***,* ***David Morgan,*** Cardiff University, UK

As XPS systems become ever more user-friendly, with "load-point-click-report" type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

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[2] R. McLaren, G. Owen and D. J. Morgan, "Analysis Induced Reduction of a Polyelectrolyte", Results in Surfaces and Interfaces, (2021) 100032
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4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed,*** National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene's inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 "Surface Chemical Analysis".

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Biomaterial Interfaces Division
Room 318 - Session BI+AS+HC+SS-MoA

Bioinspired Materials and Applications

Moderators: Sally M. McArthur, Deakin University, Australia, **Tobias Weidner**, Aarhus University, Denmark

1:40pm **BI+AS+HC+SS-MoA-1 Bioinspired Approaches to Prevent Microbes and Fouling on the Surface of Membranes***, R. Shah, T. Goodwin, **Jessica Schiffman,*** University of Massachusetts Amherst **INVITED**

The reliability and ease of operation of membrane-based water purification systems has led to their increased use in water and wastewater treatment. However, water and energy are mutually dependent critical resources; to produce clean water requires energy and the production of energy requires large volumes of water. Unfortunately, when microorganisms and other foulants accumulate on the surface of membranes and block their pores, more energy is required to operate the separation process even though its productivity is significantly reduced. The overall goal of this talk is to illustrate how bioinspired approaches can be used to enhance the properties of ultrafiltration membranes. Our first approach will demonstrate how we controlled the deposition of the bioinspired "glue" dopamine in order to fabricate ultrafiltration membranes with retained selectivity and pure water flux. Molecules for polymerization were immobilized on the membrane's surface yet prevented from attaching to the membrane's pores due to a backflow of nitrogen gas achieved using simple in-house constructed equipment. If time allows, I will provide an overview of our recent exploration into how pitcher plant inspired immobilized liquids can dramatically increase the fouling resistance of membranes that have consistent flux over at least ten cycles of operation. Biofouling during membrane-based operations is a major challenge and we suggest that there are numerous bioinspired approaches that can address this problem.

2:20pm **BI+AS+HC+SS-MoA-3 Antibiotic-Free Liquid Layers Decrease Bacterial Adhesion on Catheters In Vivo***, C. Fong,* University of Maine*; M. Andersen, A. Flores Mireles,* Notre Dame*; **Caitlin Howell,*** 5737 Jenness Hall

The rise of antibiotic resistance is one of the greatest global public health challenges of our time. Although new antibiotics continue to be discovered, the pace is slowing while the rate of discovery of new antibiotic-resistant organisms continue to grow at an alarming rate. New, non-chemical approaches are needed which can reduce bacterial surface attachment and growth without leading to further resistance. Over millions of years, Nature has developed several ways to mechanically direct or stop bacterial growth, leading to materials-based antibacterial mechanisms which are elegant, effective, and difficult for bacteria to overcome. One of these approaches, immobilized liquid layers, functions via the use of a mobile, dynamic, and sacrificial physical barrier between the bacteria and the surface which they may contaminate. *In vitro* proof-of-concept experiments using urinary catheters— one of the most common and infection-prone medical devices—liquid layers were found to reduce bacterial adhesion by 99% compared to untreated controls. In tests *in vivo*, the system performed beyond expectations, reducing not only bacterial adhesion but overall surface protein contamination as well. The results provide hope that continuing to engineer materials-based approaches to stop bacterial adhesion and growth can help us to stay ahead of antibiotic resistance.

2:40pm **BI+AS+HC+SS-MoA-4 Discovery of Cell Instructive Materials for Next Generation Medical Devices: Exploring Microtopography and 3D Shapes***, **Morgan Alexander,*** University of Nottingham, UK

The polymer biomaterials found in the clinic today are dominated by materials that have been chosen largely on the basis of their availability and mechanical properties. It would be desirable to design our way forward from this situation to new and better biomaterials chosen for positive interactions with surrounding cells and tissues. Unfortunately, our understanding of the interface between most materials and biology is poor. Only in isolated cases is there a good understanding of cell-material surface interactions and fewer still where material-tissue interactions are well characterised and understood.

This paucity of information on the mechanism of biomaterial interactions within the body acts as a roadblock to rational design. Consequently, we have taken a high throughput screening approach to discover new bio-instructive polymers from large chemical libraries of synthetic monomers presented as micro arrays. [1,2] This approach, akin to engineering serendipitous discovery, has resulted in novel materials which we have taken all the way from the lab to the clinic.

More recently we have extended our approach to explore the opportunities offered by micro topography and 3D shape manipulation to provide bio-instructive cues topography to immune cells, stromal cells and pathogenic bacterial cells. To do this we have developed and adopted a range of high throughput screening platforms, including theTopoChip[3], ChemoTopoChip [4] and used 3D printing to produce the ArchiChip [5]. The talk will focus on these topographic platforms and our findings, in particular novel topographies that reduce bacterial biofilm formation and provide beneficial host cell responses which has the potential to reduce infection in medical device implantation.[6]

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[5] Innate Immune Cell Instruction Using Micron-scale 3D Objects of Varied Architecture and Polymer Chemistry: The ChemoArchiChip Vassey et al. under review.

[6] Micro topographical instruction of bacterial attachment, biofilm formation and in vivo host response Romero et al. under review.

3:00pm **BI+AS+HC+SS-MoA-5 Development of a Method for Visualizing Nanometer-Scale Three-Dimensional Structures of Chromosomes by Three-Dimensional Atomic Force Microscopy***, **Ryohei Kojima**, K. Miyazawa, K. Teramae,* Kanazawa University, Japan*; T. Sumikama,* PRESTO, JST, Japan*; M. Meguro,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Imadate,* Osaka University, Japan*; N. Okano,* Kanazawa Unversity, Japan*; S. Horike,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Hirahara,* Osaka University, Japan*; T. Fukuma,* Kanazawa University, Japan

Three-dimensional atomic force microscopy (3D-AFM) is capable of obtaining 3D force images at solid-fluid interface in sub-nanometer scale. In the previous research, 3D-AFM visualized molecular-scale hydration and flex molecular structures of bio samples such as lipid and DNA. As a next step, it is required to visualize 3D complex structures with high order molecular organizations.
In this research, we developed 3D-AFM for visualizing 3D folded structures of human chromosomes. Chromosome (Fig. 1a) is composed of 3D folded structures that has important roles for genetic transfer. However, nanometer-scale 3D folded structures of human chromosomes have not been well understood yet. It is expected that 3D-AFM contributes to chromosome study, but it is difficult to measure inside of 3D folded structures of chromosomes by conventional conical tip without damage of samples by tip scanning. To visualize 3D folded structures of chromosome by 3D-AFM, we fabricated a carbon nanotube (CNT) tip (length > 500 nm, diameter < 20 nm) to penetrate chromosomes by 3D-AFM. By using the conventional tip and home-made CNT tip (Fig. 1c(i)-d(i)), we performed 3D-AFM of human chromosomes, and obtained 3D frequency shift (Δf) image (Fig. 1b). We extracted single Δf curves from the 3D Δf images obtained with Si tip and CNT tip, respectively (Fig. 1c(ii)-d(ii)). Δf curve using CNT tip shows oscillatory profile until 500 nm in depth from the surface of the chromosome in contrast to the Δf curve using Si tip. This result suggests that the obtained 3D Δf image using CNT tip reflects structures inside chromosome. Based on this research, applications of 3D-AFM will be expanded for visualizing 3D structures of biological samples in various research fields.

3:20pm **BI+AS+HC+SS-MoA-6 Mass-Manufactured Surface Textures Kill Bacteria as Part of Low-Cost Water Purification Devices***, **Liza White**, C. Howell,* University of Maine

Water purification and disinfection, particularly of turbid water, is a significant and growing need worldwide. Pulsed electric field (PEF) devices can be used to inactivate pathogens in water; however, manufacturability, power consumption, cost, and portability remain significant hurdles. Through leveraging paper industry technology in Maine, we have optimized electric field generation using custom textured film in a roll-to-roll manufacturing process to act as the functional part of portable PEF water purification devices. Specifically, we used commercially produced textured release paper as a substrate for the film electrodes and explored different types of metal coating to reduce the overall power consumption, cost, and manufacturability. CAD and modeling software was then used to simulate various textures to determine the optimal texture to focus the electric field while keeping a low total current density, and a custom texture was designed. The mass-manufactured textured materials were cut into singular flow cells and were sputter-coated with various metals and assembled. The flow cells were connected to a pulsed generator that pulsed a square wave at 15 µs at a frequency of 100 Hz with a voltage of 100 V. Water with a known concentration of bacteria was pushed through the flow cells at a rate of 200 µL/minute. The outlet sample was collected, and bacterial reduction was calculated. These tests demonstrated that mass-manufactured surface textures could function as part of a low-cost PEF water purification device. The development of low-cost PEF water purification devices based on surface texture will help provide more accessible clean water in the face of growing water shortages.

4:00pm **BI+AS+HC+SS-MoA-8 Nature-inspired Materials for Energy and Environmental Sustainability***, **Tak Sing Wong**,* The Pennsylvania State University **INVITED**

With an evolutionary history of 3.95 billion years and over 8 million species on earth, natural organisms have often served as blueprints for the design of highly functional engineered materials. In particular, natural species have demonstrated how different micro/nanoscale surface architectures can yield an array of distinct interfacial functions. Understanding the fundamental principles behind these natural surfaces will aid the design of multifunctional materials for a range of energy and sustainability applications. In this talk, I will discuss a number of specific examples showcasing our recent biologically inspired technologies which take inspirations from insects to plants. These examples include the development of anti-fouling and self-cleaning surfaces inspired by the slippery rims of the *Nepenthes* pitcher plants, as well as the fabrication of ultra-antireflective coatings inspired by the leafhopper-produced brochosomes. Perspectives on how nature-inspired materials may impact future applications in energy and sustainability will be discussed.

4:40pm **BI+AS+HC+SS-MoA-10 Programmable Biomimetic Light-Harvesting Systems: Quantum-Optical Control of Light-Matter Interactions***, A. Lishchuk, E. Csanyi, **Graham Leggett**,* University of Sheffield, UK

The absorption of light by molecules leads to the formation of excitons (electron-hole pairs). Control of excitons is essential for many new and emerging technologies, but the inefficient dynamics and short diffusion lengths (~ 10 nm) of excitons in molecular systems limit their utilisation.Theory suggests that exciton diffusion lengths could be enhanced by several orders of magnitude in the strong light-matter coupling regime. However, design principles for the production of photonic materials that exploit strong coupling are lacking. We have found that photosynthetic light-harvesting complexes (LHCs) from plants and bacteria are strongly coupled to localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures, yielding macroscopically extended excited states that enable coherent, non-local excitation transfer and the creation of bespoke optical states not found under weak coupling. However, proteins are not suitable for putative applications of molecular photonic materials. Inspired by photosynthetic LHCs, we demonstrate the fabrication of programmable plexcitonic antenna complexes, in which polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling, yielding delocalised excited states (plexcitons) that extend across at least 1000s of pigments. In our plexcitonic antenna complexes, poly(amino acid methacrylate) scaffolds grown from gold nanostructures by atom-transfer radical polymerisation (ATRP) organise excitons (transitions in chlorophylls) within LSPRs to achieve strong light-matter coupling, yielding Rabi energies up to twice as large as those achieved with biological LHCs. The energies of the resulting delocalised excited states (plexcitons) are programmed by varying the degree of polymerisation, scaffold packing density and chlorophyll loading. Steric hinderance in fully-dense PCysMA brushes limits binding of bulky chlorophylls, but the chlorophyll concentration can be increased to ~2M, exceeding that in biological light-harvesting complexes, by controlling the grafting density and polymerisation time. Moreover, synthetic plexcitonic antenna complexes display pH and temperature responsiveness, facilitating active control of strong plasmon-exciton coupling. These biologically-inspired metamaterials offer great promise for the design of new types of molecular photonic device.

5:00pm **BI+AS+HC+SS-MoA-11 Microfluidic QCM with Ultrahigh Q-Factor: A New Paradigm for Acoustic Biosensing?***, Y. Zhao,* Duke University*; Z. Parlak,* Qatch LLC.*; M. Yu,* Duke University*; D. French,* Qatch LLC.*; W. Aquino, **Stefan Zauscher**,* Duke University

Acoustic thickness shear mode transducers, such as the quartz crystal microbalance (QCM), can provide high throughput biomolecular detection for diagnostics with minimal sample preparation. A QCM's resonance frequency change (Δf) is generally related to the mass change (Δm) due to analyte binding on the sensor surface. If equipped with dissipation monitoring, a QCM's dissipation (D or ΔD) is related to the viscoelastic properties of the surface-bound analyte. Although current QCM sensors are simple and robust devices, they generally require high sample volumes and suffer from low sensitivity/resolution due to fluid damping.

We show that by adding microfluidic channels onto QCM sensors, we can strongly couple small amounts of liquid within the channels to the sensor, thereby largely eliminating fluid damping. This coupling eliminates dissipation effects during shear excitation and thus dramatically increases the quality factor (Q-factor) of the sensor and allows for accurate measurement of changes in fluid density, and therefore also for biomolecular mass measurements in liquid environments.

The abrogation of damping effects arises from the almost lossless coupling of the liquid to the side walls of the channels, which results in an in-plane pressure wave. We found that if the wavelength of the pressure wave is considerably longer than the channel width, the liquid inside the channels is strongly coupled to the channel walls and thus damping is suppressed. Since viscous effects are largely eliminated, the microfluidic QCM (µ-QCM) is also insensitive to temperature-induced viscosity changes. With a high Q-factor, direct data interpretation, pure mass sensitivity and temperature insensitivity, and small device size, the µ-QCM provides a new paradigm for acoustic biosensing.

We used Finite Element Analysis (FEA) to test our hypothesis that the in-plane pressure wave generated by the channel side walls is responsible for the enhanced performance of the µ-QCM. Furthermore, we conducted a nondimensional analysis to reveal the most important parameters, including channel dimensions, crystal thickness, and fluid viscosity/density, and how they affect the dissipation. This knowledge can be easily extended to other acoustic bio-transducers to improve their sensitivity/resolution.

Finally, we show the design and microfabrication of µ-QCM devices, and their testing with a range of liquids with known viscosity and density, to demonstrate the high Q-factor of µ-QCMs and to demonstrate the latter's ability to sense density changes (unencumbered by viscosity) in small (~nL) sample volumes.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-MoA

Advances in Materials and Analysis in Heterogeneous Catalysis I

Moderators: Dan Killelea, Loyola University Chicago, **Swetlana Schauermann**, Christian-Albrechts-University Kiel, Germany

2:00pm **HC+AS+SS-MoA-2 Electrocatalytic Activity of Size-Selected Sub-Nano Pt Clusters Toward the Hydrogen Evolution Reaction**, ***Tsugunosuke Masubuchi,*** University of Utah; *S. Kumari, Z. Zhang, P. Sautet, A. Alexandrova,* University of California at Los Angeles; *H. White, S. Anderson,* University of Utah

Platinum is known to exhibit high electrocatalytic activity toward the hydrogen evolution reaction (HER). From a sustainable point of view, sub-nano Pt clusters can be promising HER electrocatalysts because their electrochemically active surface area per mass is much larger than that of bulk Pt or larger Pt nanoparticles. There are fundamental questions, however, about the nature of the HER mechanism, including the electronic and structural properties of the catalytic sites required.

To this end, we studied the HER activity of atomically size-selected sub-nano Pt clusters deposited on conductive oxide supports. The electrodes of sub-nano Pt clusters were prepared using a home-built cluster beam deposition instrument, which consists of a laser vaporization cluster source, a mass-selecting ion beamline, and an ultrahigh vacuum (UHV) end station for cluster deposition. The oxide substrates were cleaned in advance by Ar^+ sputtering and annealing and tested to ensure that they are electrochemically inactive. Ions of size-selected sub-nano Pt clusters were deposited on the substrates until a certain coverage was reached. The sample electrodes prepared in this way were exposed to an O_2-free $HClO_4$ electrolyte solution, and electrochemical measurements were performed.

In this contribution, we will discuss how every Pt atom counts for the HER activity of size-selected sub-nano Pt clusters. We will particularly show that by the interplay between the experiment and quantum chemical calculations, certain Pt clusters, composed of only several atoms, can reduce protons and adsorb hydrogen atoms very efficiently, which leads to their superior HER activity.

2:20pm **HC+AS+SS-MoA-3 In situ X-ray Absorption Spectroscopy to Probe the Dynamics of Ni_3Fe catalysts: Implications for Dry Methane Reforming**, *L. Cruz,* University of California, Riverside; *J. Hong,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; *S. Shah,* University of California - Riverside; *S. Bare,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; ***Kandis Leslie Gilliard-AbdulAziz,*** University of California - Riverside **INVITED**

The exsolution of nanoparticles from perovskite precursors has been explored as a route to synthesize firmly anchored catalysts. The characteristics of these exsolved nanoparticles, such as size, composition, and morphology, are highly dynamic depending on the redox nature of the reactive environment. Their dynamic nature warrants a study that tracks the changes with in-situ and ex-situ characterization to benchmark states. In this talk, we will discuss the use of operando X-ray Absorption Spectroscopy (XAS) to study the formation, evolution, and regeneration of exsolved NiFe nanoparticles from $LaFe_{0.8}Ni_{0.2}O_3$ perovskite oxide precursors. STEM-HAADF with EDS analysis was used to measure the nanoparticle composition and morphology after exposure to dry methane reforming (CH_4, CO_2, CO, H_2, H_2O), reductive (H_2) or oxidative (O_2) conditions. Our findings show that the nanoparticle formation in 5%H_2/He occurs in sequential exsolution mechanisms where Ni exsolves first and then Fe. During DRM conditions, the Ni composition transforms from predominantly Fe-rich to Ni-rich NiFe catalysts. Lastly, we will discuss the regeneration of bimetallic alloys and implications for future work in exsolved bimetallic alloys.

3:00pm **HC+AS+SS-MoA-5 Photocatalysis between High-Purity and Applied Reaction Conditions: Understanding Carbon Dioxide Reduction on the Molecular Level**, ***Jennifer Strunk,*** Leibniz Institute for Catalysis, Germany **INVITED**

Reducing carbon dioxide just with the energy of (sun)light to platform chemicals for the chemical industry (e.g. carbon monoxide, methane) is still a highly desirable process to enable a recycling of this greenhouse gas. Yet, despite more than 40 years of research, the achievable yields in photocatalytic carbon dioxide reduction have not increased significantly, thereby clearly failing to meet demands for industrial implementation. One significant hurdle is our limited understanding of the chemical processes on the molecular scale, in particular under reaction conditions relevant to a future application. This is to a large extent due to the vastly different, and in part badly described, reaction conditions applied in published works, making it practically impossible to compare the different studies.

Our approach is the design of a reactor and a research methodology to enable highly reproducible studies in photocatalytic carbon dioxide reduction. Using solely construction parts suitable for high vacuum applications, we have developed the so-called "high-purity gas-phase photoreactor" with gas chromatographic trace gas analysis, allowing to obtain reproducible results on the ppm level. It can also function as bridge between true single-crystal studies and possible reaction conditions in practical applications.

Using this device, fair comparisons of different photocatalysts suggested in literature has been possible. This revealed the well-known titanium dioxide as one of the best materials, despite its large bandgap. Reliable apparent quantum yields have been determined. Focusing our studies on titania, it has been possible to obtain a rather complete picture of the reaction progress on the molecular scale. The reaction from carbon dioxide to methane is likely not a linear sequence of reduction steps but involves also oxidative steps by a reaction with holes. Even if methane as one-carbon product is formed, intermediates involving a C-C bond are involved. The limiting step is the water oxidation reaction, which does not run to completion. Instead, oxygen-related species are stored on or in titania until the material is saturated and the reaction ceases. These findings indicate that (i) completely other materials, possibly Z scheme systems with suitable cocatalysts, need to be developed that allow a less complex surface reaction pathway, and (ii) that (biogenic) methane may be a better co-reactant than water in a "photo dry reforming" reaction.

4:00pm **HC+AS+SS-MoA-8 Electrocatalytic Nitrate Reduction: Controlling Adsorbate Affinity to Tailor Reaction Products**, ***Kelsey Stoerzinger,*** Oregon State University **INVITED**

The electrochemical nitrate reduction reaction (NO_3RR) represents a distributed approach for water treatment and chemical synthesis (ammonia) as an alternative to conventional carbon-intensive processes

(Haber-Bosch). Catalysts requirements for this reaction, however, are immense: water/protons are required to reduce nitrate but compete with NO_3RR to evolve hydrogen gas at comparable potentials, and selectivity along an 8 e^-/10 h^+ process is required to produce ammonium. Here we investigate NO_3RR activity and ammonium selectivity across 3d and select 4d transition metals in neutral conditions prototypical of nitrate-containing source waters, developing fundamental understanding of the competitive processes that give rise to these trends to guide future catalyst design. We develop a microkinetic model capturing the potential-dependent nitrate rate order, arising from competitive adsorption between nitrate and hydrogen. Competition with the hydrogen evolution reaction is manifest in the NO_3RR Faradaic efficiency, described by catalyst work function. Selectivity to ammonium nominally increases as transition metal d-band center energy approaches and overcomes the Fermi level, with Co representing an optimal catalyst. Density functional theory calculations identify a Sabatier-like relationship between ammonium selectivity and the driving forces for nitrite reduction to nitric oxide and the dissociation of nitric oxide, where Co represents a local optimum between these two processes. These results identify competing design considerations – linking electronic structure to mechanistic selectivity-limiting steps – offering strategies to improve existing catalysts and design new alloy compositions for NO_3RR to ammonium.

4:40pm **HC+AS+SS-MoA-10 Energetics and Growth Modes of Ni and Pd Nanoparticles on Graphene / Ni(111)***, **Kun Zhao**, J. Rumptz, N. Janulaitis, C. Campbell,* University of Washington

The use of carbon supports for late transition metal nanoparticle catalysts has grown substantially in recent years due to efforts to develop electrocatalysts for clean energy applications and catalysts for new aqueous-phase biomass-related conversions, and due to the evolution of new carbon materials with unique properties (e.g., graphene, carbon nanotubes, etc.). However, much less is known about the bonding energetics of catalytic metal nanoparticles on carbon supports in comparison with oxide supports, which are more common for thermal catalysis. Here we investigated the growth morphologies and heats of adsorption of Ni and Pd vapor deposited onto graphene/Ni(111) at 300 K and 100 K using He^+ low-energy ion scattering (LEIS) and single crystal adsorption calorimetry (SCAC). For Ni/graphene/Ni(111), the SCAC results showed at 300 K the heat of adsorption of Ni vapor increases rapidly from 336 kJ/mol initially to the heat of sublimation (430 kJ/mol) by 2 ML, and at 100 K from 230 kJ/mol to the heat of sublimation slower by 3.5 ML. The growth models derived from LEIS results suggested that Ni grows as flat-topped islands with a thickness of ~1.5 nm when deposited at 300 K, and small hemispherical cap shape with a number density of 2×10^{16} particles/m^2 when deposited at 100 K. The particle size and morphology account for the differences in the heat of adsorption versus coverage at these two temperatures. The Ni chemical potential as a function of average particle diameter in the 0.5 to 4 nm range at 100 K was determined from the LEIS and SCAC measurements, and an adhesion energy of 3.6 J/m^2 was determined from fitting the chemical potential vs diameter to a theoretical model. For Pd/graphene/Ni(111), the heats of adsorption of Pd increase with coverage similarly to Ni at 300 K and 100 K and reach the heat of sublimation (370 kJ/mol) by 2.8 ML, with an initial heat of adsorption at 300 K (272 kJ/mol) that is 47 kJ/mol higher than at 100 K. The trends in the heat of adsorption are supported by the growth model from the LEIS results. Similar to Ni growth, however with much smaller particle size and larger particle density, Pd grows as flat-topped islands at 300 K with a thickness of ~0.85 nm, and hemispherical cap shape at 100 K with a number density of 6×10^{16} particles/m^2. The evolution of Pd chemical potential along with particle size was determined in the average particle diameter range of 0.6 – 2.5 nm at 100 K and the adhesion energy was found to be 3.8 J/m^2.

5:00pm **HC+AS+SS-MoA-11 Size Dependent CO_2 Reduction Activity and Selectivity of Ag Nanoparticle Electrocatalysts in sub-5 nm Regime***, **Xingyi Deng**,* NETL/LRST*; D. Alfonso,* NETL*; T. Nguyen-Phan,* NETL/LRST*; D. Kauffman,* NETL

Coinage metals (Au, Cu and Ag) are state-of-the-art electrocatalysts for the CO_2 reduction reaction (CO_2RR). Size-dependent CO_2RR activity of Au and Cu has been studied, and increased H_2 evolution reaction (HER) activity is expected for small catalyst particles with high population of undercoordinated corner sites. A similar level of consensus is lacking for Ag catalysts because the ligands, capping agents, or stabilizers typically used to control particle size and crystallographic orientation can block specific active sites and mask inherent activity trends. We used a combination of ultrahigh vacuum surface science techniques, electrochemical measurements, density functional theory, and microkinetic modeling to finely resolve the size dependent CO_2RR activity and selectivity of Ag nanoparticle electrocatalysts in the sub-5 nm range. Experimental results identified CO_2RR selectivity increased with average particle diameter between 2 to 6 nm with 3.7 ± 0.7 nm diameter Ag particles demonstrating the highest combination of CO_2RR activity and selectivity. A nearly identical size-dependent trend was also predicted in computational modeling: smaller diameter particles favored H_2 evolution reaction (HER) due to a high population of Ag edge sites, whereas larger diameter particles favored CO_2RR as the population of Ag(100) surface sites grew. Our results resolve the CO_2RR behavior of Ag in the crucial sub-5 nm range and establish an effective minimum size limit for balancing activity and selectivity. Particles below a critical diameter suffered from poor selectivity, while larger particles above the critical diameter demonstrated bulk-like activity that led to reduced catalyst utilization. These results provide insight into the size-dependent CO_2RR activity of pristine Ag catalysts and will help guide future catalyst development efforts.

Manufacturing Science and Technology Group

Room 305 - Session MS+AP+AS+TF-MoA

Advanced Characterization and Metrology for 3D and ML for Microelectronics Materials Discovery

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Jeremy Mehta**, U.S. Department of Energy

1:40pm **MS+AP+AS+TF-MoA-1 Semiconductor Metrology for Dimensional and Materials Scaling***, **Bryan Barnes**,* NIST **INVITED**

Dimensional and materials scaling are two key drivers for advancing computational capabilities beyond the conventional scaling trends of the last several decades. Future device metrology solutions must be developed now without clarity as to which combinations of proposed architecture(s) and novel materials will prove best suited for integration into high-volume manufacturing. This presentation briefly reviews these possible pairings and the near-term and long-term metrology challenges as identified in the *IEEE International Roadmap for Devices and Systems*. As device dimensions further approach near-atomic and atomic scales, many of the several existing metrology techniques will face new tests, illustrated here using examples and solutions from our optics-based semiconductor metrology research. No single metrology technique can address all issues faced in modern process control and inspection; thus we address complementary techniques across semiconductor metrology are required to address dimensional and materials scaling

2:20pm **MS+AP+AS+TF-MoA-3 Towards a Digital Twin for Spatiotemporal Experiments***, **Subramanian Sankaranarayanan**,* Argonne National Laboratory **INVITED**

We will present our ongoing efforts at creating a virtual platform or "DigitalTwin", wherein the users can exhaustively explore experimental controls and obtain synthetic read-outs – a small subset that displays the most interesting physics and/or phenomena can be explored in the actual experiments. We take advantage of the fact that most experimentalspatiotemporally-resolved measurements at SUFs in real or reciprocal space can be derived from the accurate prediction of atomic configurations and their dynamical evolution across time- and length. We will use representative examples to demonstrate how Digital Twins can be utilized for accelerated materials discovery and design.

3:00pm **MS+AP+AS+TF-MoA-5 Autonomous Scanning Probe Microscopy: from Streaming Image Analysis to Learning Physics***, S. Kalinin, **Yongtao Liu**,* Oak Ridge National Laboratory **INVITED**

Machine learning and artificial intelligence (ML/AI) are rapidly becoming an indispensable part of physics research, with domain applications ranging from theory and materials prediction to high-throughput data analysis. However, the constantly emerging question is how to match the correlative nature of classical ML with hypothesis-driven causal nature of physical sciences. In parallel, the recent successes in applying ML/AI methods for autonomous systems from robotics through self-driving cars to organic and inorganic synthesis are generating enthusiasm for the potential of these techniques to enable automated and autonomous experiment (AE) in imaging.

In this presentation, I will discuss recent progress in automated experiment in scanning probe microscopy, ranging from real-time image segmentation to physics discovery via active learning. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. I will further illustrate transition from post-experiment data analysis to active learning process, including learning structure-property relationships and materials discovery in composition spread libraries. Here, the strategies based on simple Gaussian Processes often tend to produce sub-optimal results due to the lack of prior knowledge and very simplified (via learned kernel function) representation of spatial complexity of the system. Comparatively, deep kernel learning (DKL) and structured Gaussian Processes methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of ferroelectric domain dynamics in piezoresponse force microscopy. For probing physical mechanisms of tip-induced modifications, I will demonstrate the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed.

4:00pm **MS+AP+AS+TF-MoA-8 New in-Line Metrology for Advanced Semiconductor Nodes***, **Cornel Bozdog**,* Onto Innovation **INVITED**

Scaling in Semiconductor Device Manufacturing means "more devices per unit area". The traditional "device shrink" scaling path was already replaced by "stack vertically" in non-volatile memory devices, now up to few hundred devices occupying the same real estate on the wafer, and growing. Gate all-around allowed logic devices to stack multiple transistors, and volatile memory is following suit. Different devices and sub-devices are now bonded together to further optimize scaling. To integrate, optimize and control the multi-thousand-step manufacturing line, in-line metrology plays the critical role. Here we will review the metrology challenges for Advanced 3D devices, present the latest advancements in traditional optical, scatterometry, electron-beam and atomic force techniques, and discuss novel x-ray, acoustic, and mid-IR metrology solutions that enable accurate profile reconstruction, in-device characterization and hybrid metrology schemes.

4:40pm **MS+AP+AS+TF-MoA-10 Applications of Artificial Intelligence AI and Machine Learning ML to Semiconductor Materials Discovery and Optimization***, **Brian Valentine**,* DOE **INVITED**

Semiconductor elements such as silicon and gallium are applied in a wide variety of electronic, optical, and energy conversion applications; new elemental, compound, and dopant compositions are continually sought to improve known semiconductor characteristics to find unknown but desired semiconductor material characteristics. In this paper some applications of AI and ML to semiconductor material design and optimization are reviewed, along with limitations of AI and ML techniques applied to materials design and development and forward directions in these materials design and development methods.

Nanoscale Science and Technology Division
Room 304 - Session NS1+AS+EM-MoA

Correlative Microscopy for Nanoscale Characterization

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Georg Fantner**, EPFL, Switzerland

1:40pm **NS1+AS+EM-MoA-1 Large Volume 3D Biological Imaging with Electron and Cryo-Super-Resolution Microscopy***, **Harald Hess**,* HHMI, Janelia **INVITED**

Volume or 3D electron microscopy continues to expand its potential for imaging ever larger biological entities while preserving a best compromise step edge isotropic resolution of 5-10 nm. This was driven by the challenge of imaging the entire fly brain in sufficient detail for extracting the circuitry of connectome. While the resolution is not of the standards of TEM's, such resolution is of unique value when it encompasses whole cells and complete tissues.We will review the capabilities of FIB-SEM, with ~100 micron sized volumes. Numerous examples can be browsed on openorganelle.com . A cryogenic protocol involving sample vitrification, cryogenic imaging by structured illumination or by photoactivated localization microscopy then followed by staining and resin embedding can then produce the sample suitable for further FIBSEM imaging. This effectively adds protein location information as a color to the 3D EM image. Likewise, several examples correlating specific proteins in the nucleus, on membranes, on and defining organelles and vesicles. Prospects of future challenges are discussed. We will also describe a system capable of imaging volumes approaching 1 mm^3 It is based on Ion Beam Etching and Milling with a Multi beam Scanning Electron MicroscopeIBEaM MSEM.

2:20pm **NS1+AS+EM-MoA-3 The Role of SnO_2 Processing on Ionic Migration in Multi-Halide Perovskites***, **Holland Hysmith**,* University of Tennessee Knoxville*; S. Park,* National Renewable Energy Laboratory*; A. Ievlev, Y. Liu,* Oak Ridge National Laboratory*; K. Zhu,* National Renewable Energy Laboratory*; M. Ahmadi,* University of Tennessee Knoxville*; J. Berry,* National Renewable Energy Laboratory*; O. Ovchinnikova,* Oak Ridge National Laboratory

Moving towards a future of efficient, accessible, and less carbon reliant energy devices has been at the forefront of energy research innovations for the past 30 years. Multi-halide perovskite (MHP) thin films have gained significant attention due to their flexibility of device applications and tunable capabilities for improving power conversion efficiency.[1] Many behavioral aspects to MHP's are thoroughly investigated: functionality of grain boundaries, recombination effects, ionic migration patterns, and hysteresis.[2-4]

Chemical Vapor Deposition (CVD) is a widely used technique for thin film coatings due to its ability for producing high volume batches of MHP's with larger grain sizes, fewer defects, and fewer grain boundary formations.[5-6] Additionally, nanoparticle processing has been applied to induce enlargement of grain boundaries, showcasing larger current signals than its MHP counterparts.[7] Therefore, how does common substrate processing techniques (i.e. CVD, nanoparticles, hybrid) influence the behavior of MHP phenomenon such as ion migration and grain boundary formation? Speculated as inducing ionic recombination and driving I-V hysteresis in MHP's, understanding how chemistry can be tuned to reduce such effects would be optimal.[8-9]

We demonstrate how a hybrid approach of CVD and nanoparticle SnO_2 substrate processing significantly improves the performance of $(FAPbI_3)_{0.97}(MAPbBr_3)_{0.03}$ perovskites in comparison to each technique utilized on its own. As shown in **Figure 1**, higher performing hybrid devices exhibit fused grain boundary formations, not seen in exclusive CVD or nanoparticle devices. Conductive Atomic Force Microscopy (c-AFM) was used to track fused boundary locations and differentiate them from topographic features. Such fusing behavior has been previously observed to showcase higher counts of current and reduce defects such has halide vacancies.[7]

In summary, to understand the chemistry behavior with respect to each device interface, Time of Flight Secondary Ionization Mass Spectrometry (ToF-SIMS) depth profiling was applied. Demonstrated in **Figure 2**, migration of K^+, Na^+, Ca^+, FA^+, MA^+ was found in hybrid devices, in addition to Ca^+ and Na^+ clustering on the perovskite/air layer. Salt clustering could be correlated to the fusing effect demonstrated in the surface morphology imaged in c-AFM. Presence of K^+ has shown to reduce defects driven by alkali iodides like NaI^- and Ca^+ can help with enlarging the bandgap layer in studies where Ca+ was used to replace Pb^+.[10-11] Furthermore, reduced separation between positive ion such as MA^+ and FA^+ from negative ions can decrease the potential responsible for I-V hysteresis.[12]

2:40pm **NS1+AS+EM-MoA-4 Nanoplastic Arrays – from Chaotic Measurements to New Order***, A. Madison, D. Westly, R. Ilic, C. Copeland, A. Pintar, C. Camp, J. Liddle, **Samuel M. Stavis**,* National Institute of Standards and Technology (NIST)

Nanoplastic particles are ubiquitous contaminants of the environment, and their unknown hazards are of deepening concern. Optical microspectroscopy is essential to elucidate the structure–property relationships of nanoplastic particles. However, a lack of standards that are fit for purpose limits the reliability of such measurements, resulting in a growing spate of chaotic reports. In particular, the default standard of a colloidal suspension has disadvantages, with sample preparation typically resulting in disordered arrays of nanoparticles with uncontrolled sizes on imaging substrates. Moreover, existing nanoplastic standards can have broad and asymmetric distributions of optical properties. This issue confounds inference of dimensional properties and requires further study.

Optical microspectroscopy often involves contrast from Rayleigh scattering, fluorescence emission, and Raman scattering to detect, quantify, and identify nanoplastic particles. Numerous issues limit accuracy, including optical responses that vary with nanoparticle dimensions and imaging systems that present aberration effects. These issues require standards that provide reference values of dimensional, optical, and positional properties. The latter issue is unexplored, motivating a new order of microscopy standards.

We introduce the concept of the nanoplastic array, addressing these issues. This prototype standard enables calibration, correction, and correlation of image data from multiple instruments, improving the accuracy of microspectroscopy measurements. To prove the concept, we fabricate nanoplastic arrays in nanoscale films of phenolic resin by electron-beam lithography, including both fluorescent dopants and sorbents to study optical properties that are indicators of chemical sorption and resulting hazards.

Our nanoplastic arrays feature three types of nanostructures. The simplest is a uniform film, enabling correction of non-uniform irradiance for the accurate analysis of fluorescence intensity, and providing reference spectra for Raman measurements. Building in complexity, arrays of uniform pillars provide reference dimensions and positions to correlate and calibrate multiple imaging modes. Finally, and most complex, variable pillar arrays facilitate measurements of optical properties as a function of dimensional properties, with fine gradations of pillar diameter enabling quantification of the limits of detection.

Nanoplastic arrays will enable new accuracy and reliability in optical microspectroscopy, advancing the quantitative study of nanoplastic contaminants to transform unknown hazards into known quantities.

3:00pm **NS1+AS+EM-MoA-5 Development of Nanoendoscopy-AFM for Visualizing Intracellular Nanostructures of Living Cells*, Keisuke Miyazawa,*** Kanazawa University, Japan*; M. Penedo,* EPFL, Switzerland*; N. Okano, H. Furusho, T. Ichikawa, M. Shahidul Alam, K. Miyata,* Kanazawa University, Japan*; C. Nakamura,* AIST, Japan*; T. Fukuma,* Kanazawa University, Japan

Atomic force microscopy (AFM) is the only technique that allows label-free imaging of nanoscale biomolecular dynamics, playing a crucial role in solving biological questions that cannot be addressed by other major bioimaging tools (fluorescence or electron microscopy). However, such imaging is possible only for systems either extracted from cells or reconstructed on solid substrates. Thus, nanodynamics inside living cells largely remain inaccessible with the current nanoimaging techniques. Here, we overcome this limitation by the nanoendoscopy-AFM, where we fabricate a needle-like nanoprobe (diameter < 200 nm, length > 500 nm) made of Sillicon or Carbon, and insert it into a living cell directly in order to measure a force curve, and visualize 2D or 3D internal structures of living cells by the measured 3D force applied to the tip during three-dimensional tip scanning. By using this method, we measured the 3D force image of a human cancer cell (HeLa). The result clearly shows the nucleus in the living cell. In addition, our results using the developed nanoendoscopy-AFM showed undetectable changes by the previous methods such as actin fiber three-dimensional (3D) maps, and 2D nanodynamics of the membrane inner scaffold in the living cells. Unlike previous AFM methods, the nanoprobe directly accesses the target intracellular components, exploiting all the AFM capabilities, such as high-resolution imaging, nanomechanical mapping, and molecular recognition. These features of the nanoendoscopy-AFM should greatly expand the range of intracellular structures observable in living cells, and contribute to the various life science research fields.

Plasma Science and Technology Division
Room 315 - Session PS+AS-MoA

Plasma Chemistry and Catalysis

Moderators: Michael Gordon, University of California at Santa Barbara, **Floran Peeters**, LeydenJar Technologies, Netherlands

1:40pm **PS+AS-MoA-1 Study of Plasma-Catalyst Surface Interactions for Nitrogen Oxidation*, Michael Hinshelwood,*** *Y. Li, G. Oehrlein,* University of Maryland College Park

Cold atmospheric pressure plasma is a promising tool for enhancing thermal catalysis for nitrogen fixation through NO_x formation. Reactive species generated in the plasma are thought to stimulate reactions at the catalyst surface, but the specific interactions are not well understood. We use a plasma-catalysis setup that enables study of such interactions by infrared spectroscopic methods [1]. In this work the formed species of N_2-O_2 interactions in plasma and over a Pt-Al_2O_3 catalyst are analyzed. An N_2/Ar gas stream is flown through an atmospheric pressure plasma jet (APPJ) to the heated catalyst in a confined chamber, and unexcited N_2 or O_2 gas can also be admitted downstream from the plasma source to the catalyst surface. Catalyst surface species are analyzed using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase species exiting the catalyst bed are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Plasma power, catalyst temperature and Ar/N_2 flow are varied to investigate plasma-catalyst interactions. Bare Al_2O_3 is additionally analyzed as a reference material to isolate the effects of the catalyst from the support. Results reveal multiple interactions on the catalyst surface. Downstream gas FTIR shows a slight increase (40%) of total N_xO_y species upon heating the catalyst from 25 ^{o}Cto 350 ^{o}C suggesting an increase in reactive nitrogen or oxygen species. Additionally, N_2Odecreases upon heating while NO_x densities rise. The catalyst also promotes oxidation of NO to NO_2 compared to the support-only case at 350 ^{o}C, a known feature of platinum catalysts.DRIFTS data reveals that the Al_2O_3 support acts to store NO_x species below 450 ^{o}C through the formation of surface nitrites and nitrates, necessitating the use of long exposure times. Correlations of downstream FTIR and DRIFTS data will be presented to untangle various interactions and isolate the processes resulting in plasma catalysis. We thank B. Bayer, Dr. A. Bhan and Dr. P. J. Bruggeman for helpful discussions. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

2:00pm **PS+AS-MoA-2 Investigation of the Interaction Between Non-Thermal Plasma Activated Nitrogen and Metal Surfaces*, Garam Lee,*** *C. Yan, W. Schneider, D. Go, C. O'Brien,* University of Notre Dame

Non-thermal plasma (NTP)-assisted catalysis has recently gained substantial interest in the heterogeneous catalysis field for enhancing catalytic activity and/or selectivity, as well as for enabling chemical transformations that neither plasma nor catalysis could deliver individually. Despite the promise, the influence of NTP activation of molecules on reactivity at a catalytic surface remains primitive. Here, we report observations of the products and reactivity of plasma-activated nitrogen (N_2) species exposed to polycrystalline Ni, Pd, Cu, Ag, and Au surfaces using a newly-designed multi-modal spectroscopic tool that combines polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS), mass spectrometry (MS), and optical emission spectroscopy (OES), combined with density functional theory (DFT) models to rationalize those observations. Observations and models indicate that NTP activation provides access to metastable surface nitrogen species that are inaccessible thermally. Those metastable species are characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), temperature-programmed desorption (TPD), and temperature-programmed reaction (TPR) with hydrogen (H_2) to produce ammonia (NH_3). Models and observations highlight dependence of this reactivity on the identity of the metal surface. Taken together, results shed light on the role of NTP activation on promotion of surface reactivity.

2:20pm **PS+AS-MoA-3 Long-Term Degradation of PTFE in a Low Temperature Oxygen Plasma*, Tobias Wagner,*** *T. Zeller, M. Rohnke, J. Janek,* Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

Atomic oxygen (AO) is the most common gas species in the Low-Earth-Orbit (LEO) and responsible for material degradation of the outer shell of satellites and spacecrafts within this space region. As the LEO is also essential for commercial space flights, the degradation process of materials exposed to AO needs to be better understood in order to prevent possibly devastating material failure. Due to its properties, low temperature oxygen plasmas are suited for material degradation studies taking place on earth instead of quite expensive space studies. Here we focus on the long-term degradation of Polytetrafluoroethylene (PTFE), which is often employed on the outside of spacecrafts and therefore exposed to AO. Up to date, there is no complete understanding of the degradation process on the molecular level, which is necessary for materials improvement and new materials development.

For the degradation studies, a self-constructed capacitively driven 13.56 MHz RF reactor was used to generate an oxygen plasma for the simulation of LEO conditions. PTFE was characterised in the pristine state and after AO treatment at different times by ToF-SIMS, XPS, SEM and confocal microscopy. During plasma treatment, the samples show a linear mass loss behaviour. ToF-SIMS surface analysis reveal mass fragments like COF^- or C_3O^+, which shows a clear chemical reaction of oxygen species with PTFE. The presence of these molecular indicators was verified by XPS, where additional carbon and oxygen species were found after treatment. SEM micrographs showed an inhomogeneous degradation on the surface in the first hours similar to actual LEO exposure. For a complete understanding of the degradation progress, mass spectrometric studies of the plasma composition are carried out in situ. Overall, the results show that the reaction of PTFE with AO is occurring on a chemical rather than a physical path, with the fragmentation of long carbon chains into smaller fragments likely driving the material degradation.

2:40pm **PS+AS-MoA-4 Study of Elastomer Degradation in Processing and Cleaning Plasma Chemistries***, **Nicholas Connolly**, D. Barlaz, R. Garza, D. Ruzic, M. Sankaran,* University of Illinois Urbana-Champaign*; N. Kolliopoulos, G. Lunardi,* DuPont Precision Parts & Solutions

Fluoroelastomer (FKM) and perfluoroelastomer (FFKM) materials are used extensively in seals for plasma processing equipment used to manufacture semiconductors. Chamber etching and cleaning processes, particularly those using fluorine chemistry, oxygen chemistry, or a mixture of both, lead to the degradation of the elastomer seals. While most decomposition products are volatile, the recognition of seals as a source of chamber contamination in the form of undesired etch products and particle generation is important for robust semiconductor manufacturing processes. Recent emphasis on coatings and filler materials for elastomer seals makes understanding of decomposition conditions an ongoing effort.

This work investigates the relationship between plasma parameters, including electron temperature, plasma density, and radical densities, and elastomer seal degradation in mixtures of $SF_6/O_2/Ar$ plasmas. Various commercial FKM/FFKM materials will be investigated. Langmuir probe analysis is used to characterize electron temperature and density (predicted T_e of 3 eV and density of 1×10^{17} m^{-3}), while in-situ thermocouple-based radical probes are used to measure radical densities of oxygen. Efforts towards the development and implementation of an in-situ fluorine radical probe will also be reported. Characterization of the elastomer surface after plasma exposure will be completed using electron microscopy and optical profilometry, as well as testing of mechanical properties of the seals.

3:00pm **PS+AS-MoA-5 Utilizing Optical Spectroscopy to Explore Mechanisms of Plasma-Assisted Catalysis in Model Exhaust Systems***, **Joshua Blechle**,* Wilkes University

With increasing concerns over the environmental presence of nitrogen oxides, there is growing interest in utilizing plasma-mediated conversion techniques. Nonthermal plasma-assisted catalysis (PAC) in particular has shown great potential for continued improvements in exhaust abatement. Advances, however, have been limited due to a lack of knowledge in regards to the fundamental chemistry of these plasma systems, and the complexity of the plasma-surface interface. The sheer number of potential catalysts and the variability in exhaust gas composition further exacerbate these issues.

In order to investigate these interactions, a number of inductively-coupled plasma systems were generated from model exhaust precursors (notably, N_2 and O_2 mixtures). Internal energies of notable diatomic species are determined via optical emission spectroscopy (OES) to explore the trends in energy partitioning with respect to plasma conditions. Repeated measurements in the presence of precious metal (Ag, Pt, and Pd) and alumina surfaces demonstrate a strong vibrational temperature (T_V) dependence with respect to applied power (25-200 W) but a somewhat limited dependence on substrate identity. In addition, very little change in N_2* and N* densities are observed, whereas there are significant decreases in both NO* and O* densities in the presence of all substrates. A series of composite (Ag/γ-Al_2O_3) catalysts with varying Ag loading are also studied, with T_V's ranging from ~2500-5100 K, with the highest temperatures reached for raw alumina systems, demonstrating a Ag-mediated vibrational quenching.

To further explore catalytic behavior, kinetic trends are observed via time-resolved OES, with rate constants determined for both the formation and destruction of relevant excited states. Correlating these data with measured densities and temperatures allows for unique insight into the plasma-surface interface and the mechanisms by which these processes occur. Expanding upon the library of system conditions and increasing the complexity of the exhaust gas model will serve as a foundation for improved design and implementation of PAC methods.

3:20pm **PS+AS-MoA-6 Gasification of Carbon and CO_2 Into CO at Low Vacuum Through Combined Plasma and Heating Exposure***, **Edwin Devid**,* DIFFER, Netherlands*; R. Van de Sanden,* DIFFER & EIRES, Netherlands*; M. Gleeson,* DIFFER, Netherlands

Atmospheric CO_2 concentrations still continue to rise in 2020 [1] and are threatening the goals of the Paris Agreement [2]. By activating CO_2 through plasma, CO_2 is reduced into CO where CO is not only a high-value chemical for the chemical industry but also allow to store renewable electricity into chemical energy via an intermittent way at the cost of CO_2 consumption. Currently, mere CO_2 dissociation through non-thermal inductively coupled Radio Frequency (RF) plasma is not economically viable to obtainboth high CO_2 conversion and energy recovery efficiencies [3,4].

In this experiment, CO_2 dissociation by plasma is assisted by the co-reactant carbon. Through this co-reactant, additional processes will take place that aids the CO_2 dissociation into CO. In low vacuum (~1.3 mbar CO_2), carbon is heated (till 1000 K, in a quartz tray) while being exposed to CO_2 plasma. This process gives increased yields of CO where O_2 gas is consumed by the dominating process: $2C + O_2 \rightarrow 2\,CO$. No evidence of the gas phase back reaction $CO + 1/2O_2 \rightarrow CO_2$ is observed. By usage of isotopic carbon^{13} and modeling of the mass spectrometric data, the different processes operating (i.e. $2C + O_2 \rightarrow 2\,CO$ versus $CO_2 \rightarrow CO + 1/2O_2$ and $CO_2 + C \rightarrow 2\,CO$) are disentangled. Under a buildup ~1.3 mbar CO_2 atmosphere plus combined plasma and heat exposure upon the carbon gives, with increasing temperature a steeply rising of emitted CO at the cost of declining O_2 and CO_2. From the isotopic carbon is determined that after plasma and heat exposure: the surface color, surface area and pore volume has been changed. In addition the sample mass is reduced (carbon consumption up to 36% gravimetrically), confirming that carbon is consumed.

This potentially opens a new way toward O_2 removal during CO_2 dissociation processes by combining plasma with heating of carbon to generate a clean CO_2/CO stream. If the carbon is of a biogenic origin, the process as a whole is sustainable and fossil free CO is generated. Other additional processes that aid to further increase the CO yield (like reverse Boudouard reaction: $CO_2 + C \rightarrow 2\,CO$) help to find ways for industry to reach higher CO yields by both increasing the CO_2 conversion and the consumption of O_2 through the presence of carbon via non-thermal plasma.

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[2] C. Streck et al., Journal for European Environmental & Planning Law, (2016). 13. 3-29.

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4:00pm **PS+AS-MoA-8 Investigation of Oxygen Permeation Enhancement with He/O_2 Plasma and SOEC Interaction***, **Xingyu Chen**,* Dutch Institute for Fundamental Energy Research, China*; F. Peeters, F. Smits, W. Bongers, R. van de Sanden,* Dutch Institute for Fundamental Energy Research, Netherlands

High temperature solid-oxide electrolysis cells (SOECs) using oxygen-selective conducting membrane in combination with plasma has shown high conversion efficiencies in nitrogen fixation and CO_2 conversion, which provides a promising method for renewable energy usage and gas conversion. But the underlying kinetics and limiting rates of the plasma-assisted oxygen conducting membrane remain not clear. The plasma-activated species (e.g., by plasma-excitation, dissociation and ionization) may promote the reduction kinetics on the ion-conducting membrane surface. The effects of plasma-induced surface charging and local fields on the exchange kinetics may also play a significant role in the improvement of the oxygen permeation fluxes of the ion-conducting membrane. To understand the interaction of the plasma and the oxygen-conducting membrane, we develop a dedicated plasma-SOEC reactor to investigate the plasma enhanced oxygen permeation mechanism.

In this contribution, we will present the experimental results of the enhancement of the oxygen permeation fluxes owing to the presence of the oxygen radicals and electrons from He/ O_2 low pressure (~1 Torr) plasma. Langmuir probe measurements and optical emission spectrometry and actinometry will determine the plasma properties (electron density, electron temperature and O radical densities etc.) and provide inputs for the plasma-kinetic modelling of the plasma bulk and wall region. The characterizations of the SOEC with different plasma conditions and membrane temperature are conducted to determine the pumping rates (current density) of the oxygen permeation process. Ultimately, the plasma effects on SOEC performance will be quantified, and novel insights into the ion-conducting rate-limiting kinetics will be discussed.

4:20pm **PS+AS-MoA-9 Application of Plasma-Liquid Chemistry to Carbon-Carbon Bond Formation via Pinacol Coupling Reaction*, Scott Dubowsky*,** *J. Wang,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; J. Moore, M. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas in contact with liquids have attracted interest for various chemical applications including the degradation of organic pollutants,[1] conversion of abundant feedstocks,[2,3] and more recently, organic chemistry.[4] Compared to other chemical approaches, plasma-liquid chemistry does not require a catalyst material, is electrified, and produces unique reactive species such as solvated electrons, one of the strongest chemical reducing species.[5]

We present an application of plasma-liquid chemistry to the building of carbon-carbon bonds via the well-known Pinacol coupling reaction. In this organic reaction, a carbonyl group is reduced, typically by an electron donating catalyst such as magnesium, to form a ketyl radical anion species. A pair of these ketyl groups then react to form a vicinal diol, which in the presence of a proton donor such as water, leads to the final diol product. Here, we show that the Pinacol coupling reaction is successfully carried out at a plasma-liquid interface without any catalyst. Our study was performed with a direct-current (DC) powered plasma operated in a previously reported electrochemical setup and primarily focused on methyl-4-formylbenzoate (MFB) as the substrate. For an initial concentration of 0.12 M and a constant operating current of 2.3 mA, the yield of the Pinacol product increased with time from 6.1% after 1 h to 34% after 8 h, while the faradaic efficiency correspondingly decreased from 85.7% to 54.2%. Based on nuclear magnetic resonance (NMR) spectroscopy, methyl 4-(dimethoxymethyl)benzoate and 4-(methoxycarbonyl)benzoic acid were also generated as side products. By carrying out scavenger control experiments, we show that the vicinal diol is produced by solvated electron reduction. Finally, we have extended the application of plasma-liquid chemistry to Pinacol coupling of several other aromatic aldehydes and ketones to emphasize its generality.

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4:40pm **PS+AS-MoA-10 Understanding Temperature Inhibition of Methane Conversion in DBD Plasma Using Electrical Characterization and Optical Emission Spectroscopy*, Ibukunoluwa Akintola*,** *G. Rivera-Castro, J. Yang, J. Hicks, D. Go,* University of Notre Dame

Non-thermal plasmas (NTPs) produce highly reactive chemical environments made up of electrons, ions, radicals, and vibrationally excited molecules. These reactive species, when combined with catalysts, can help drive thermodynamically unfavorable chemical reactions at low temperatures and atmospheric pressure. We are particularly interested in the direct coupling of light hydrocarbons (e.g. methane) and nitrogen to produce value-added liquid chemicals (e.g. pyrrole and pyridine) in a plasma-assisted catalytic process. In order to effectively create these plasma catalytic systems, it is imperative that there is a fundamental understanding of the plasma-phase chemistry alone. While there have been many studies on nitrogen (N_2) and methane (CH_4) plasmas, there is limited understanding on how changing operating conditions (i.e. feed ratio, plasma power, operating temperature) affect the plasma properties and ensuing plasma chemistry. In this work, we characterize the plasma using electrical measurements and optical emission spectroscopy (OES) and analyze the chemical products using gas chromatography to understand the effects, if any, of varying plasma parameters on product formation. Relevant electrical properties and thermodynamic information such as electron density, vibrational and rotational temperatures, as well as the presence of key plasma species (C-N, C-H, N_2) are compared to relevant products formed during plasma-alone reactions. Results show that different operating conditions lead to changes in energy partitioning in the reaction. Specifically, an increase in temperature leads to a reduction in methane conversion which appears to have an inverse relationship with the vibrational temperatures of C-H species in the plasma.

5:00pm **PS+AS-MoA-11 Optimization of CO_2 Dissociation Efficiency and Conversion in Vortex-Stabilized Microwave Plasmas by Effluent Nozzles*, Cas van Deursen*,** DIFFER, Netherlands*; H. van Poyer,* DIFFER, Belgium*; Q. Shen,* DIFFER, China*; W. Bongers,* DIFFER, Netherlands*; F. Peeters,* Technical University of Eindhoven, Netherlands*; F. Smits, R. van de Sanden,* DIFFER, Netherlands

Efficiency and conversion in a reverse vortex microwave plasma utilized for CO_2 dissociation are enhanced by considering and optimizing the thermal trajectory of the plasma effluent using a Laval nozzle. The nozzle is used to mix the cold, unconverted gas at the edges of the tube with the hot, dissociated gas in the middle of the flow and to force the gas to accelerate, thereby cooling the effluent. The temperature trajectory of the gas is determined by measuring the gas temperatures of the plasma core and the afterglow using OES and the gas exiting the Laval nozzle using a thermocouple. The effects of the nozzle on the size of the plasma is determined using OES and plasma imaging. The effects of different nozzle diameters on the temperature trajectory and conversion and efficiency are compared to the baseline configuration. Measurements show significant improvements in energy efficiency at close to atmospheric pressures (500 – 900 mbar), especially for higher flows (12 – 18 slm). Results are discussed and explained on the basis of simulations. Options for further improving reactor efficiency and conversion are also discussed.

Surface Science Division
Room 319 - Session SS+AS-MoA
Molecular Organization at Surfaces

Moderator: Donna Chen, University of South Carolina

2:40pm **SS+AS-MoA-4 Protein Structure and Dynamics at the Air-Water Interface Using Sum Frequency Generation Simulations*, Kris Strunge*,** Aarhus University, Denmark*; Y. Nagata,* Max Planck Institute for Polymer Research, Germany, Denmark*; T. Weidner,* Aarhus University, Denmark

Protein function and folding are perturbed by the presence of interfacial environments. Many protein is active at an interface making it most relevant to study these molecular systems right at the interface. However, the study of the topmost monomolecular layer is made difficult by the high of amount of solvated protein in close proximity to the interesting interfacial species. This calls for spectroscopic methods like sum frequency generation (SFG) spectroscopy, which is inherently surface sensitive from its selection rules and allow studies of the molecularity at the interface based on the vibrational spectrum coming specifically from the interface probing molecular orientation, structure dynamics and interactions. However, extracting this information from the SFG spectrum a challenge due to the non-linear phase sensitive interference affecting the spectrum which can be solved by relating experimental SFG spectra with accurate spectra calculation based on molecular simulation.Wewant to show how information from SFG spectroscopy can be coupled with molecular dynamics simulation to resolvemolecular orientation, dynamics and interactions of proteins at interfaces.

The sum frequency spectrum of the LTα14 peptide shows a characteristic amide I peak at 1640 cm^{-1}signifying the expected α-helical structure, but more specific informationlike interactions with per residueresolution and the nature of their vibrations at the interface is gained bycalculating the SFG spectrum based on state-of-the-art velocity-velocity time correlation functions sampled through molecular dynamics simulation. With this tool we can learn how the frequencies of each individual amino acid residue contributions and inter-residue coupling lead to the inhomogeneous broadening of the surface specific vibrational spectrum. For example, we can learn thatα-helical peptides lying flat on an interface mainly interacts withsurface withthe residues on the side of the helix. The top and bottom positioned residues are more rigid and despitethe bottom residues' close proximity to the surface, they are not as highly perturbed by the presence of the interface.

Furthermore, SFG allowsus to probe the influence of interfacial proteins on the water structure and the vibrational response of interfacial water as the spectra simulations is easily transferred to other molecular systems of interest in the scientific community.

3:00pm **SS+AS-MoA-5 Confinement at Solid-solid Interfaces Enhances Crystallinity of COF Thin Films***, **Joshua Roys**[1], J. O'Brien, N. Stucchi,* Clarkson University*; A. Hill,* St. Lawrence University*; J. Ye, R. Brown,* Clarkson University

The condensation reaction of covalent organic frameworks (COFs) on the mica surface demonstrated enhanced crystallinity when physically confined by an exfoliated graphene capping layer. This talk discusses the impact of confinement at a solid-solid interface on two-dimensional COF growth at the solid-solid interface. Understanding confined COF behavior could inform new applications, such as the integration of 2D COFs into 2D van der Waals materials as intercalated layers. The growth of 2D COFs was characterized at the mica-graphene interface by atomic force microscopy (AFM), micro-Fourier transform infrared spectroscopy (micro-FTIR), and density functional theory (DFT). At temperatures sufficient for reaction, AFM topographic and phase imaging observed long-range crystalline growth on the order of square micrometers in graphene-confined domains. Domains outside of the exfoliated graphene flakes did not exhibit long-range mesoscale structural order and retained similar morphology to pre-annealed structures. Micro-FTIR spectra confirmed COF formation both under and outside graphene confinement, as well as an increased presence of trapped water beneath graphene after reactive annealing. Diffusion barriers estimated by DFT calculations suggested the enhanced crystallinity of confined COFs was not the result of heightened mobility of confined molecules or non-covalent self-assembly. The increased COF crystallinity when confined by a graphene layer most likely originated from enhanced dynamic covalent crystallization due to prolonged exposure to water trapped beneath the graphene flake during the annealing process. This behavior should be universal for condensation-reaction covalent organic frameworks formed under confinement at solid-solid interfaces.

3:20pm **SS+AS-MoA-6 Metal Tetraphenylporphyrin Induced Organic/Metal Interactions***, **Isheta Majumdar**, F. Goto, A. Calloni, M. Finazzi, L. Duò, F. Ciccacci, G. Bussetti,* Politecnico di Milano, Italy

The field of organic electronics has seen the emergence of engineered hybrid metal electrode/organic molecule interfaces where molecules can be ordinally assembled in 2D scalable devices. Metal surfaces can be screened (passivation) by single atomic layers, namely, ultra-thin metal oxide layers, in view of preserving the molecular electronic properties when deposited on the underlying substrate [1].

In the present work, one such system studied is the passivated iron, known as Fe(001)-*p*(1 × 1)O (preparation protocol in [2]), with a metal tetraphenylporphyrin (MTPP) overlayer deposited under ultra-high vacuum, using a molecular beam epitaxy system. The sample is characterized by ultraviolet photoelectron spectroscopy (UPS) and low energy electron diffraction (LEED). We have observed that transition MTPP (M= Co, Ni, Pt, Pd) deposition on Fe(001)-*p*(1 × 1)O have resulted in the same *commensurate* (5 × 5)R37° superstructure (37° rotation w.r.t. the main Fe crystal), as observed by LEED pattern. ZnTPP and CdTPP are the only exceptions, which exhibit regular (5 × 5) symmetries, while Fe(Cl)TPP and CuTPP show mixed LEED patterns (presence of overlapping regular and rotated superstructures). This occurrence drove a detailed investigation to find possible strategies (surface engineering) to obtain a specific molecular superstructure.

Therefore, in the next phase of our study, mixed M_1TPP + M_2TPP monolayers were grown sequentially at room temperature by depositing *x* ML of M_1TPP on Fe(001)-*p*(1 × 1)O followed by (1-*x*) ML of M_2TPP (Fig. 1). The corresponding UPS characterization (Fig. 1 (i)) confirms the monolayer coverages of the mixed MTPP layers. In Fig. 1 (ii), top row: CoTPP (M_1TPP) is deposited first (*x* = 0.25), followed by ZnTPP; bottom row: ZnTPP (M_1TPP) is deposited first (*x* = 0.25), followed by CoTPP. It is observed that the growth of a CoTPP "seed" is able to stabilize a ZnTPP (5 × 5)R37° ordering, not observed on a pure ZnTPP layer. Conversely, a ZnTPP “seed” results in a mixed LEED pattern, where CoTPP molecules retain their characteristic (5 × 5)R37° ordering. This occurrence indicates that there is a significant influence of one type of MTPP over the other that determines the surface reconstruction.

Furthermore, in another set of mixed MTPP depositions, nominally equal amounts of ZnTPP and CoTPP where grown by means of co-deposition on Fe(001)-*p*(1 × 1)O. In this case, CoTPP showed a certain dominance while influencing the resultant surface reconstruction of the mixed MTPPs. 0.50 ML CoTPP and 0.50 ML ZnTPP co-deposition resulted in a (5 × 5)R37° ordering (Fig. 1 (iii)).

4:40pm **SS+AS-MoA-10 Characterization of Oxygen Evolution from Rh(111)***, **Maxwell Gillum**, E. Jamka, C. Grytsyshyn-Giger, F. Lewis, A. Kerr, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

5:00pm **SS+AS-MoA-11 Developing a Mechanistic Understanding of Nb_3Sn Growth: Sn Adsorption and Diffusion Behavior on (3×1)-O Nb(100)***, **Rachael Farber**,* University of Kansas*; S. Willson,* University of Chicago*; A. Hire, R. Hennig,* University of Florida*; S. Sibener,* University of Chicago

Niobium (Nb) is the current standard material for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance and high cavity quality factor (*Q*) at operating temperatures of ~ 2 K. The prohibitively expensive operating and infrastructure costs of these facilities prevent the implementation of accelerator-based technologies across a variety of sectors. Nb_3Sn is a promising next-generation material for SRF cavities due, in part, to an elevated operating temperature of ~ 4.2 K.This significantly reduces the required cryogenic infrastructure and associated operating costs.

Nb_3Sn films are currently grown *via* Sn vapor deposition on preexisting Nb cavities. It is understood that the thickness of the native Nb pentoxide (Nb_2O_5), Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high *Q* film growth.There is not, however, an understanding of the Nb_3Sn growth mechanism resulting in optimal film formation. In this work, we have used a combination of *in situ* ultra-high vacuum (UHV) techniques to visualize Sn adsorption and diffusion behavior on (3×1)-O Nb(100) at the nanometer scale. Scanning tunneling microscopy (STM) data revealed preferential adsorption of Sn along the (3×1)-O unit cell with Sn diffusion guided by the underlying oxide surface as well. Annealing the Sn/Nb(100) sample resulted in the formation of hexagonal and rectangular Sn adlayer structures for all sub-monolayer (sub-ML) and ML Sn coverages studied. Genetic algorithm calculations and DFT based descriptors identified energetically preferred Sn binding sites on the (3×1)-O surface.Calculated STM images corroborated experimentally determined Sn adsorption structures for sub-ML Sn coverages. This spatially resolved, mechanistic information of Sn adsorption and diffusion on an oxidized Nb surface guides the development of predictive Nb_3Sn growth models needed for the further optimization of Nb_3Sn growth procedures.

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[1] **SSD Morton S. Traum Award Finalist**

Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EM+HI+PS+SS+TF-TuM

Area Selective Processing and Patterning II

Moderators: Michelle Paquette, University of Missouri-Kansas City, **Christophe Vallee**, SUNY College of Nanoscale Science and Engineering

8:00am **AP+AS+EM+HI+PS+SS+TF-TuM-1 New Precursors and Approaches to ALD and AS-ALD of Metals*, Mikko Ritala,*** University of Helsinki, Finland **INVITED**

Metal ALD is a topic where high technological relevance combines with inspiring and challenging scientific questions. As always, the success of ALD builds on chemistry. There is constant need for new precursors enabling ALD of metals of interest with improved characteristics. A major challenge arise from the strong tendency of metals to agglomerate, hence preventing achieving continuous films at the smallest thicknesses. Lowering of the deposition temperature is of utmost importance to limit the agglomeration. This requires highly volatile and reactive metal precursors and reducing agents. 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ((Me_3Ge)DHP) is a new reducing that is found more efficient than its earlier reported silicon analogue. $NiCl_2(PEt_3)_2$ in turn represents a series of metal halide adduct compounds of nickel and cobalt where the poorly volatile parent halides are made volatile by proper adduct ligands. The $NiCl_2(PEt_3)_2$ - (Me_3Ge)DHP combination affords deposition of Ni at 110 °C which is the lowest temperature for thermal ALD of Ni so far. (Me_3Ge)DHP enables also deposition of gold. This is the first reductive thermal ALD process of gold.

Area-selective ALD of metals is an important topic for self-aligned thin-film patterning. An entirely new approach to this is area-selective etching of polymers. In these etching processes the selectivity arises from the materials underneath the polymer layers. Both O_2 and H_2 can be used as an etchant gas. Etching gas molecules diffuse through the polymer film, and if they meet a catalytic surface underneath, the molecules become dissociated into their respective atoms which then readily react with the polymer etching it away. On noncatalytic surfaces the polymer film remains. When combined with area-selective ALD, self-aligned etching of polymers opens entirely new possibilities for the fabrication of the most advanced and challenging semiconductor devices. An example is given where the area-selective etching of polyimide from Pt was followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator (polymer)-on-insulator.

8:40am **AP+AS+EM+HI+PS+SS+TF-TuM-3 Comparing Interface and Bulk Physicochemical Properties of TiO_2 Deposited by PEALD Assisted by Substrate Biasing on Thermal SiO_2 and TiN Substrates, for Area Selective Deposition Application*, Jennifer Not,*** LTM - MINATEC - CEA/LETI, France*; L. Mazet,* STMicroelectronics, France*; T. Maindron,* Minalogic, France*; R. Gassilloud,* CEA-LETI, France*; M. Bonvalot,* LTM - MINATEC - CEA/LETI, France

To bypass the limitations implied by the miniaturization of electronic components, area selective deposition (ASD) is becoming a key point of focus, as photolithography steps are avoided. This bottom-up promising technique, as opposed to the top down approach inherent to etching, relies on nucleation mechanisms resulting from substrate - precursor interactions. Differing nucleation kinetics may indeed be observed under very same experimental conditions,[1] allowing a growth delay on a surface type while simultaneously promoting growth on a different surface.

Atomic Layer Deposition (ALD) remains a technique of choice to obtain area selective deposition. Based upon the self-limiting nature of surface reactions, this technique enables a conformal deposition with atomic-scale thickness precision, and is gradually becoming a major deposition process in the microelectronic industry.

The ALD reactor used in this study includes an ICP deported plasma source and is equipped with an additional RF polarization kit at the back side of the chuck, enabling plasma ion extraction from the source towards the substrate surface. Depending on the ion incident kinetic energy, which can be tuned as a function of the applied polarization bias, this ion flux can modulate the properties of the thin film under growth, opening new perspectives of physicochemical properties. These properties may also vary according to the substrate surface, making this RF polarization kit an interesting experimental knob for the development for ASD processes[2]. PEALD TiO_2 layers of various thicknesses have been deposited with no air break on a 15 nm-thick TiN layer, as well as on a 100 nm-thick thermal SiO_2 substrate, under various polarization bias power from 0 W to 80 W. The purpose of this work is to physically and chemically characterize the obtained thin films with respect to substrate surface, and to understand how these properties evolve with the film thickness and for various bias values. X-Ray Reflectivity (XRR), Grazing Incident X-Ray Diffraction (GIXRD), *in-situ* and *ex-situ* ellipsometry and Angle Resolved X-ray Photoelectron Spectrometry (AR-XPS) measurements have been performed, providing detailed information on chemical bond formation during nucleation and within the bulk TiO_2 layer, and thin film physical properties, such as thickness, density, roughness and crystallinity. The outcome of this study gives some insight into the benefit of bias for area selective deposition of TiO_2 thin films on TiN against SiO_2.

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9:00am **AP+AS+EM+HI+PS+SS+TF-TuM-4 Area Selective Atomic Layer Deposition of SnO_2 as An Etch Barrier*, Xin Yang,*** University of Texas at Austin*; B. Coffey,* Lam Research Corp*; J. Ekerdt,* University of Texas at Austin

Reactive ion etching (RIE) is widely used in semiconductor nanofabrication processes since it can provide high etch rate, high selectivity, and high anisotropy. Traditional etch masks such as organic photoresists suffer from shortcomings such as low etch selectivity. Other material systems have been investigated to improve the selectivity. $Sn^{(0)}$-containing block copolymers were demonstrated as materials for nanolithographic applications.

Here we propose SnO_2 as a RIE etch mask in fluorine-based etching processes. Tin forms nonvolatile compounds with fluorine enabling tin to function as an etch mask. We establish processes that create SnO_2 grid patterns, which can be transferred into the Si native oxide substrate using SF_6 RIE. The concept is illustrated using a 1000-mesh copper TEM grid as an ultraviolet light shadow mask to generate patterns in polystyrene. SnO_2 patterns are achieved by area selective atomic layer deposition (ALD) using tetrakis(dimethylamino) tin(IV) and H_2O as ALD precursors on a Si native oxide at 170 °C. The selective growth can be directed by the hydrophilicity of the substrate surface. ALD growth of SnO_2 shows no nucleation delay on Si native oxide, which is hydroxylated. By coating the substrate with a polymer such as polystyrene (PS) the reactive sites can be passivated to accomplish selective growth. SnO_2 growth can be blocked up to 50 cycles on H-terminated Si(001), and 200 cycles on cured polystyrene and possibly beyond. Atomic force microscopy (AFM) results show that SnO_2 grown on native oxide has a low roughness of 75 pm, while SnO_2 grown on H-terminated Si has a relative higher roughness of 250 pm indicating a 3-D growth process. To create SnO_2 patterns 20, 50, and 100 ALD cycles of SnO_2 are selectively deposited onto Si native oxide with estimated SnO_2 thicknesses of 1.2 nm, 3 nm and 6 nm, respectively. Samples are then etched with SF_6 RIE for 30 s to 1 min at room temperature and 200 mTorr. AFM results show that SnO_2 grid patterns are transferred into the substrate with a depth of around 300 nm to 1 µm for all three samples. X-ray photoelectron spectroscopy results show that some SnO_2 is transformed into SnF_4 for 100 ALD cycle samples, while all of the SnO_2 is transformed into SnF_4 for 20 and 50 ALD cycle samples.

9:20am **AP+AS+EM+HI+PS+SS+TF-TuM-5 Selective Deposition Two Ways: Chemical Bath Deposition of Metal Sulfides on Organic Substrates***, T. Estrada, **Amy Walker,*** University of Texas at Dallas

Selective deposition has many technological applications. While area selective deposition (ASD) has been widely investigated using atomic layer deposition (ALD), there have been few studies of composition-selective deposition or ASD in which growth occurs at material boundaries. In this talk we shall illustrate these alternate selective deposition methods using two examples.

First, we demonstrate that the composition of tin sulfides is controlled by the bath pH and the interaction of sulfur-containing species with $-CH_3$, -OH and -COOH terminated self-assembled monolayers (SAMs). On -OH terminated SAMs, as the bath pH increases from 10 to 12, the tin sulfide deposited changes from SnS_2 to Sn_2S_3. On -COOH terminated SAMs the deposit is S_2S_3 at pH 10 and SnS at pH 12. In contrast, on $-CH_3$ terminated SAMs the deposit changes from SnS at pH10 to Sn_2S_3 at pH 12. We attribute this behavior to a competition between the repulsion of the chalcogenide ions by the negatively charged carboxylic acid and hydroxyl terminal groups and an increase in chalcogenide ion concentration with increasing bath pH.

Second, we exploit the interaction of the chalcogenide ions with different SAM terminal groups to deposit CuS nanowires at the junction of micropatterned $-OH/-CH_3$ terminated SAMs. We term this method SEmiconductor Nanowire Deposition On Micropatterned substrates (SENDOM). In SENDOM the deposition reaction is kinetically favored on the $-CH_3$ terminated SAMs but transport of reactants is preferred on the hydrophilic -OH terminated SAM. Thus at short deposition times a nanowire forms at the junction of the -OH and $-CH_3$ terminated surfaces.

9:40am **AP+AS+EM+HI+PS+SS+TF-TuM-6 Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO2Films During Low-Temperature Ald on Fluorine-Rich Carbon Substrates***, **Brian Butkus**, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

A novel approach to crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and O_2 plasma. In films deposited at temperatures as low as 100 °C and with a thickness of only 4 nm, highly crystalline anatase phases have been observed. Furthermore, when deposited on glass or silicon substrates other than carbon, TiO_2 films consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

An ALD process using a Veeco® Fiji Gen2 ALD system was used to deposit TiO_2 on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 °C to 200 °C, and O_2 plasma (300 watts) and water were used as oxidants. Target film thickness ranged from 4 nm to 22 nm. To characterize the films, Raman, Fourier transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) were used. AvCarb GDS2230 substrates with an O_2 plasma as an oxidant resulted in anatase TiO_2 films irrespective of thickness, even when deposited at temperatures below 100 °C. However, the anatase phase is significantly weaker when H_2O is used as the oxidant. An interfacial layer of ALD Al_2O_3 suppresses the growth of the anatase phase. Data from XPS indicates that Ti-F bonds form at the pre-deposition stages of films with anatase TiO_2. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous TiO_2. This fluorine on the surface of the carbon paper serves as a directing agent[1-5] for the application of TTIP to PTFE in a flourolysis reaction, which drives the TiO_2 to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7]Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. With this strategy, surface initiation chemistries can be used to achieve area-selective and in situcrystallization of films.

11:00am **AP+AS+EM+HI+PS+SS+TF-TuM-10 Site-selective Atomic Layer Deposition: Targeting Electronic Defects***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We apply a selective hydration strategy to target reaction at the step edges and/or oxygen vacancies of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Al2O3 and Ga_2O_3ALD nucleation on TiO_2single crystals and MgO ALD on In_2O_3broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surface that may also act as surface or interface electronic defects.

11:40am **AP+AS+EM+HI+PS+SS+TF-TuM-12 Low Temperature Area-selective ALD and ALE of Pd***, H. Nallan, X. Yang, B. Coffey, **John Ekerdt**,* University of Texas at Austin **INVITED**

Thin film deposition and etching approaches may be constrained by the temperature limits for flexible substrates in roll-to-roll processes.We describe a low temperature ALD route to Pd metal film growth at 100 °C that uses $Pd(hfac)_2$ and H_2.The Pd ALD reaction proceeds in the presence of atomic hydrogen; Pd growth nucleates without delay on a Ni metal seed layer that catalyzes H_2 dissociation.Once nucleated, the evolving Pd surface catalyzes H_2 dissociation.To generate the Ni seed layer, a NiO film is first deposited and reduced with an atomic hydrogen source. The 100 °C ALD of NiO using bis(N,N'-di-*tert*-butylacetamidinato)nickel(II) and H_2O as coreactants is highly selective on exposed oxide surfaces and blocked on organic surfaces.NiO films as thin as 0.5 nm, once reduced to Ni^0, effectively seed Pd growth through catalytic area activation.NiO reduction employs an e-beam heated tungsten capillary at 2.5 × 10^{-6} Torr H_2 that generates atomic hydrogen to reduce NiO films at 100 °C.

In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general findings that metal oxides can be etched by a variety of vapor phase etchants, such as formic acid – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves VUV (115 nm < λ < 180 nm) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd at 100 °C.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Density functional theory is used to study the adsorption of oxidants (O and O_3) and describe O diffusion into the films to understand the kinetic limitations of the oxidation step.

Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-TuM

Synchrotron-Based Photoelectron Spectroscopy Studies of Technologically Important Materials: in Memory of David Shirley

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Eric L. Shirley**, National Institute of Standard and Technology

8:20am **AS+LS+RE+SS-TuM-2 Limitations in the Structural Determination of a Close-Packed Overlayer***, **JG Tobin**,* U. Wisconsin-Oshkosh

The close-packed metal overlayer system c(10x2)Ag/Cu(001) has been the subject of extensive electronic structure studies. These include the examination of the two dimensional behavior at low coverages, the development from two- to three-dimensionality and the convergence to three-dimensional dispersion as in Ag(111). It would be of use to have a firmer picture of the placement of the first monolayer Ag atoms (d⊥) versus the Cu(001) substrate. However, it will be demonstrated with FEFF that there are fundamental limitations to the extraction of that information with photon-induced electron diffraction. [1,2]

1. Part of the JVSTA Commemorative Volume of the Career of David A. Shirley

2. J. G. Tobin, "Limitations in the Structural Determination of a Close-Packed Overlayer,"J. Vac. Sci. Tech. A **39**, 063203 (2021), https://doi.org/10.1116/6.0001320.

8:40am **AS+LS+RE+SS-TuM-3 Sub-Micron Chemical Speciation Mapping of Uranium Dioxide Aged Under Humid Conditions***, **David Shuh**, A. Ditter, J. Pacold,* Lawrence Berkeley National Laboratory (LBNL)*; Z. Dai, L. Davison,* Lawrence Livermore National Laboratory*; D. Vine,* Lawrence Berkeley National Laboratory (LBNL)*; S. Donald, B. Chung,* Lawrence Livermore National Laboratory **INVITED**

The oxidation of uranium is a critically important process across a variety of fields. It is a key component to understanding the nuclear fuel cycle, the fate and transport of uranium in the environment, and important signatures for nuclear forensics investigations. At room temperature, the humidity of the environment is more important to oxidation than the oxygen content of the atmosphere, so understanding the uranium oxidation can offer important insights into the provenance of a specimen. The scanning transmission X-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2 is an instrument capable of chemical speciation mapping below the micron scale. Uranium oxide powder was allowed to age and agglomerate at 98% relative humidity for 378 days, then a focused ion beam (FIB) was used to section a thin slice of this agglomeration for study at the ALS STXM. Results at the oxygen K-edge and uranium N_5-edge identify a bulk, UO_2 phase and an interfacial, schoepite phase, located in distinct regions of the sample. A modified non-negative matrix factorization (NMF) method was used to separate out the primary spectral components and identify these two phases, along with a surface phase which is suspected to be water adsorbed to the surface of the sample. Use of the STXM to identify uranium phases, particularly when coupled with FIB sectioning and NMF analysis is a promising method for uranium analysis going forward.

9:20am **AS+LS+RE+SS-TuM-5 On Photoelectron Spectroscopy and the Shirley Background*, Eric L. Shirley,*** NIST **INVITED**

Photoelectron spectroscopy and allied spectroscopies, electron-yield and Auger, provide rich information about occupied and unoccupied electron states in solids. Photoelectron spectroscopy and momentum-resolved photoemission allow one to probe band structure. However, photoemission is also plagued by inelastic losses, which occur because creation of additional excitations in the sample lowers a photoelectron's kinetic energy, usually manifested in the form of "satellite peaks." This can be a nuisance in some cases, because complicated interpretation is required when analyzing photoelectron spectra, but it also affords insight into the additional excitations. Background subtraction, such as is done using, say the "Shirley background," is one method used distill spectral features. Measuring electron-yield versus photon energy can be an excellent method for obtaining x-ray absorption spectra, and this can be accomplished using the same electron analyzers as for photoemission. Auger spectroscopy is also feasible using such analyzers, and the small angular acceptance of many current analyzers at hard-x-ray photoelectron spectroscopy (HAXPES) beamlines provides Auger spectroscopy with additional insight into unoccupied states, as will be shown. In this talk, we will survey theoretical treatments applied in connection with many of the above spectroscopies, discussing both insights gained and the treatments' limitations.

11:00am **AS+LS+RE+SS-TuM-10 Origin of the Complex Main and Satellite Features in Oxides*, Paul S. Bagus,*** University of North Texas*; C. Nelin, C. Brundle, B. Crist,* Consultant*; N. Lahiri, K. Rosso,* PNNL **INVITED**

The assignment of the complex XPS features of the cations in ionic compounds has been the subject of extensive theoretical work. However, there are strong disagreements, even for the origin of the main peaks, [1-2] and the agreement with experimental observations remains insufficient for unambiguous interpretation. In particular, previous cluster model treatments were not able to properly describe the satellite features for the cation XPS. Here we present a rigorous *ab inito* treatment of the main and satellite features in the cation 2p XPS of Fe_2O_3 and NiO which resolves this problem and provides a comparable treatment of both main and satellite features. This has been possible based on a new method for the selection of orbitals that are used to form the ionic wavefunctions. This method is a state averaging of the optimized orbitals over a mixture of normal and shake configurations. The normal configurations have only an electron removed from the cation 2p shell and the shake configurations include, in addition, an electron moved from orbitals of dominantly O(2p) character into the partly filled orbitals of dominantly cation 3d character. Previous cluster model XPS studies had used orbitals optimized only for the normal configuration. [1-2] Thus, for the first time, it is possible to have a set of orbitals that can describe, with comparable accuracy, both the normal and shake configurations. [3] This is especially important since, both in the states for the main and for the satellite XPS features, the normal and shake configurations can, and often do, mix. Thus, comparable accuracy is necessary to have proper descriptions of the ionic final states. It is also important that the character of the ionic states in terms of the occupations of the open shell core and valence orbitals and of the contributions of $2p_{1/2}$ and $2p_{3/2}$ ionization to the XPS intensities have been also determined. Thus, we are able to resolve the ongoing disagreement for the assignment of some regions of the spectra to normal configurations and other regions to shake, or charge transfer, configurations. This is possible because the theoretical treatment, based on cluster models of the oxides, allows us to obtain a detailed level of information about the character of the ionic configurations.

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Biomaterial Interfaces Division
Room 318 - Session BI1+AS+EM+NS+SE+TF-TuM

Bioanalytics, Biosensors and Diagnostics

Moderators: Caitlin Howell, University of Maine, **Laura Mears**, TU Wien, Austria

8:00am **BI1+AS+EM+NS+SE+TF-TuM-1 Understanding and Employing Adhesion Forces in Microfluidic Channels for Cell Separation*, Avi Gupta,*** *F. Chrit, A. Liu, A. Alexeev, T. Sulchek,* Georgia Institute of Technology, USA

Rapid advancements in microfluidic technologies during the past few decades have significantly aided advancements in the field of BioMEMS. These technologies can facilitate development of easily scalable tools that can be translated to point-of-care healthcare products. Researchers have capitalized on these tools to create differential separation techniques that rely on adhesion forces. The adhesive interactions play a significant role in governing the trajectory of cells in microfluidic channels as well as the reliability of these devices, however, a concise model explaining cell interactions with chemically coated surfaces is yet to be developed. This research describes studies using microfluidic flow at different flow regimes to study dynamic cell adhesion. APTES, P-selectin, and Pluronic were used as models for non-specific adhesion, specific adhesion, and adhesion-free surfaces, respectively. A microfluidic device with slanting ridges was used to provide forced contact and to visualize the effect of these chemistries on cell trajectories using a microscope and a high-speed camera. Parameters of the channel that were studied include ridge angle, gap size, channel width, and flow rate. It was found that adhesive forces modulate the interaction time of cells during contact points with the slanting ridges. At an average flow velocity of 3.1 cm/sec we observed higher interaction time for APTES coatings and lower for Pluronic coatings. Higher adhesion on APTES coated surface of the channel leads to more deflection of cells towards the streamlines leading them to go opposite to the ridge direction. In contrast, lower surface adhesion on Pluronic coated surface made cells deviate along the ridge perpendicular to streamlines. Narrow channel widths and acute ridge angles helped in exaggerating the differences in trajectories of cells going along or under the ridge. Atomic force microscopy (AFM) was used to quantify the adhesion forces. This knowledge was used to develop a predictive model employing Lattice Boltzmann techniques along with Morse potential and Bell model to represent interaction between cells and device surface. This improved understanding of adhesion forces in microfluidic devices opens new avenues for developing separation techniques that don't employ specific molecules like P-selectin but rely upon the inherent geometry and surface interaction of the cells with a microfluidic channel.

8:20am **BI1+AS+EM+NS+SE+TF-TuM-2 Wafer-Scale Metallic Nanotube Arrays with Highly Ordered Periodicity for SERS Application*, Jinn Chu,*** National Taiwan University of Science and Technology, Taiwan

This paper reports on the wafer-scale fabrication of ultrahigh sensitivity SERS substrates using metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in photoresist. These include ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au). The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 10 µm) in a variety of shapes, including tall cylinders and dishes. In addition, over this is deposited a uniform coating of Au nanoparticles to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Systematic micro-Raman spectroscopic analysis reveal that the fabricated array could function as a SERS-active substrate with crystal violet (CV) and folic acid as analytes (a minimum detection limit of 10^{-13} M CV). Enhancement factor of 1.06×10^9 is obtained from our triangular Ag MeNTA. This work is the first to fabricate wafer-scale metallic nanotube arrays with SERS properties, which represents an important step toward realizing the large-scale fabrication of ultrasensitive SERS-active materials.

8:40am **BI1+AS+EM+NS+SE+TF-TuM-3 Customizing Silk Film Surface Properties Using Plasma-Enhanced Chemical Vapor Deposition***, A. Devore, G. Reyes,* ***Morgan Hawker,*** California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer with high utility in biomedical contexts, notably in tissue engineering. Silk bulk properties can be tuned to mechanically match a range of biological environments, including soft and hard tissues. As with other naturally-derived polymers, silk constructs degrade via surface-mediated enzymatic hydrolysis into non-toxic amino acid byproducts. Because tissue engineering relies on the underlying scaffold to degrade as the healthy tissue forms, controlling silk scaffold degradation kinetics is essential to maximize silk's utility. Notably, prior work to control silk degradation kinetics relies on either altering silk matrix properties (i.e., manipulating the secondary structure), or through creating silk-containing blends such as copolymers. Although both strategies effectively control degradation, doing so is often at the expense of mechanical properties. Any mechanical mismatch induced through controlling degradation can hinder scaffold function. Developing a strategy to program silk degradation - without altering bulk mechanical properties - is required to enhance their efficacy as biomaterials.

This talk will highlight recent efforts to develop a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) approach with the potential to modulate silk degradation. The long-term objective of this work is to control the rate of surface-mediated enzymatic hydrolysis by customizing silk surface properties. Surface properties are thought to be paramount in controlling silk construct/enzyme interactions, so tuning silk film surface properties using PECVD was a logical first step. Silk films were first dropcasted, and were then subjected to PECVD. Plasma feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface), and pentane (to produce thin films with non-polar functional groups on the silk surface). Plasma polymerization using mixed precursor conditions was also explored. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control silk films. Changes in surface chemistry were evaluated using high-resolution x-ray photoelectron spectroscopy. Collectively, findings demonstrated that surface properties depend on both feedgas composition and position of the silk film in the plasma reactor. In sum, PECVD represents a promising approach to customize silk surface properties.

9:00am **BI1+AS+EM+NS+SE+TF-TuM-4 Biopotential Sensing Using Flexible, Reusable Smart Textile-Based Dry Electrodes*, Jitendra Pratap Singh,*** Physics Dept IIT Delhi, India

Biopotential signals are used to assess organ function and make diagnoses. Biopotential electrodes are used to monitor and record biopotentials by acting as an interface between biological tissue and electrical circuits. The accurate detection of physiological signals from the human body is essential for health monitoring, preventive care, and treatments.

Wearable bioelectronics developments applied directly on the epidermal surface provide a promising future biopotential sensing option. Wearable textile electrodes for biopotential sensing are a promising candidate for long-term health monitoring. Wearable health-monitoring devices should be simple to use, stigma-free, and capable of delivering high-quality data. Smart textiles, which incorporate electronic elements directly into the fabric, offer a seamless way to incorporate sensors into garments for a variety of purposes. This work describes different types of flexible and reusable textile-based dry electrodes for biopotential monitoring. This work also describes the direct writing of laser-induced graphene (LIG) on a Kevlar textile for the production of reusable dry electrodes for long-term ECG monitoring. The electrode as-prepared has a high electrical conductivity and skin contact impedance of 100 ± 1 kΩ to 7.9 ± 2.7 kΩ for frequencies ranging from 40 Hz to 1 kHz, which is comparable to conventional Ag/AgCl wet electrodes.

The outcomes demonstrate comparable performance with significantly reduced electrode-skin impedance for clinical-grade devices. Even after several hours of usage, these electrodes do not irritate the skin and are effective without any skin preparation. As a result of their flexibility and a better match to the modulus of the skin, it is anticipated that the suggested dry electrodes will provide comfort for long-term biopotential monitoring. A simple, cost-effective, and scalable fabrication approach enables the fabrication of flexible electrodes of arbitrary shape for long-term biopotential monitoring.

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9:20am **BI1+AS+EM+NS+SE+TF-TuM-5 Functional Plasma Polymers for Biosensing Applications*, Melanie McGregor,*** University of South Australia **INVITED**

Materials with intricate nanostructures display wetting properties that modern technologies already use to lubricate engines or waterproof clothing. Yet, their full potential in applications for sustainable catalysis, air purification or biosensing cannot be realised until we understand how nano-objects adsorb to surfaces with features of comparable size. Indeed, controlling or even predicting how proteins, antibodies, exosomes, surfactant or nanoparticles stick to nano-engineered surfaces is a challenge because key aspects of the wetting phenomenon remain poorly understood at this scale. In this talk, I will briefly review what we currently know about "nanowetting".[1] I will then introduce the concept of plasma polymerisation as a technique to control both surface chemistry and surface topography. I'll use the example of plasma deposited polyoxazoline (POx) to highlight this technique's attributes, drawbacks and recent progress made in understanding the unique chemistry and reactivity of POx films, using both plasma in-situ and post deposition spectroscopic analysis.[2]Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non-cytotoxic and low fouling.[3] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process, which makes them particularly attractive for industrialization. For these reasons, plasma deposited polyoxazoline are used in applied biomedical research, from in vitro stem cell culture to controlling immune responses.[4]

I'll conclude this presentation with tangible outcomes of the translational research projects I've conducted with various industries, where we used nanoengineered plasma polymers, to create materials for cancer diagnosis and growing organoids.[5]

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Biomaterial Interfaces Division
Room 318 - Session BI2+AS-TuM

Characterization of Biological and Biomaterials Surfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Graham Leggett**, University of Sheffield, UK

11:00am **BI2+AS-TuM-10 Getting to the Surface of Biology*, Lara Gamble,*** University of Washington **INVITED**

A variety of different surfaces (or interfaces) exist in biology. The surface of a biomaterial is the interface between that biomaterial and the biological environment. State-of-the-art instrumentation, experimental protocols, and data analysis methods are needed to obtain detailed information about these surface and interface structures and their compositions. Surface analysis tools such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) can provide images of polymer biomaterials, cells, and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism that affect responses to chemotherapy. Since many biomaterials (e.g. porous polymer scaffolds), cells, and tissues are three-dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. However, it is challenging to characterize these topographically complex materials with surface-sensitive techniques. With the use of gas cluster ion beams (GCIBs) surface analysis tools such as x-ray photoelectron spectroscopy (XPS) and ToF-SIMS can attain very fine z-resolution (<10 nm) in-depth profiles. In this presentation, ToF-SIMS analysis of biologically relevant samples in 2D and 3D will be presented.

11:40am **BI2+AS-TuM-12 3D Investigation of Sr^{2+} Mobility in Bone Marrow by ToF- and Orbi-SIMS**, *C. Kern, A. Pauli, R. Jamous, T. El Khassawna,* ***Marcus Rohnke***, Justus Liebig University Giessen, Germany

Next generation biomaterials will be functionalised with drug release systems. In osteoporosis research strontium ions (Sr^{2+}) have emerged as promising therapeutic agent in modified bone cements for better fracture healing. In previous work we focused on the Sr^{2+} release off a functionalised bone cement and its dispersion in the mineralised areas of rat bone. [1, 2] Here, we go one step further and investigate Sr^{2+} transport within the much more complex system bone marrow in a passive dispersion experiment. First, we present an experimental cryo-workflow for transport studies within bovine bone marrow. As analytical tools for tracking the Sr^{2+} diffusion in 3D and spatially resolved characterisation of the bone marrow we apply time-of-flight secondary ion mass spectrometry (ToF-SIMS) and orbitrap secondary ion mass spectrometry (Orbi-SIMS). Within a time-dependent experimental series, the validity of our experimental approach is shown. Average diffusion coefficients of Sr^{2+} in bovine bone marrow in fast diffusion areas ($D_{\text{bovine,FD}}=(2.09\pm2.39)\cdot10^{-9}$ cm^{2}s^{-1}), slow diffusion areas ($D_{\text{bovine,SD}}=(1.52\pm1.80)\cdot10^{-10}$ cm^{2}s^{-1}), and total area diffusion ($D_{\text{bovine,TA}}= (1.94\pm2.40)\cdot10^{-9}$ cm^{2}s^{-1}) were obtained. In a subsequent proof-of-concept study, we successfully applied the developed protocol to the determination of Sr^{2+} diffusion in bone marrow of osteoporotic rats [fast diffusion: $D_{\text{rat,FD}}=(9.02\pm5.63)\cdot10^{-10}$ cm^{2}s^{-1}); slow diffusion: ($D_{\text{rat,SD}}=(6.48\pm3.88)\cdot10^{-10}$ cm^{2}s^{-1}); total area diffusion ($D_{\text{rat,TA}}= (8.89\pm5.37)\cdot10^{-10}$ cm^{2}s^{-1}]. Detailed 2D and 3D mass spectrometric imaging analysis as well as Orbi-SIMS spectral analysis revealed that Sr^{2+} diffusion is slower in bone marrow areas with high intensity of lipid and fatty acid signals than in areas with less intensity of lipid signals. Overall, our results provide important insights about Sr^{2+} diffusion in bone marrow and we are able to show that both cryo-ToF-SIMS and Orbi-SIMS are useful tools for the investigation of rapid diffusion in water-containing highly viscous media.

[1] M. Rohnke, S. Pfitzenreuter, B. Mogwitz, A. Henß, J. Thomas, D. Bieberstein, T. Gemming, S.K. Otto, S. Ray, M. Schumacher, M. Gelinsky, V. Alt, Strontium release from Sr^{2+}-loaded bone cements and dispersion in healthy and osteoporotic rat bone, J. Controlled Release **262** (2017) 159

[2] C. Kern, M. Quade, S. Ray, J. Thomas, M. Schumacher, T. Gemming, M. Gelinsky, V. Alt, M. Rohnke, Investigation of strontium transport and strontium quantification in cortical rat bone by time-of-flight secondary ion mass spectrometry, J. R. Soc. Interface **16** (2019) 20180638

12:00pm **BI2+AS-TuM-13 Comparison of NAP-XPS and Cryo-XPS for Studies of the Surface Chemistry of the Bacterial Cell-Envelope**, ***Paul Dietrich***, SPECS Surface Nano Analysis GmbH, Germany; *M. Kjærvik,* BAM Berlin, Germany, Norway; *M. Ramstedt,* Umeå University, Sweden; *W. Unger,* BAM, Germany

Bacterial interactions with the environment are based on processes involving their cell-envelope. Thus, techniques that can analyze their surface chemistry are attractive tools for providing an improved understanding of bacterial interactions. One of these tools is x-ray photoelectron spectroscopy (XPS) with an estimated information depth of <10 nm for Al Kα-excitation. XPS-analyses of bacteria have been performed for several decades on freeze-dried specimens to be compatible with the classical ultra-high vacuum conditions needed. A limitation of these studies has been that the freeze-drying method may collapse cell structure. However, recent developments in XPS allow for analysis of biological samples at near ambient pressure (NAP-XPS) or as frozen hydrated specimens (cryo-XPS) in vacuum. In this talk, we present the analysis of bacterial samples from a reference strain of the Gram-negative bacterium *Pseudomonas fluorescens* using both techniques. We will present the results obtained and, in general, observed good agreement between the two techniques. Furthermore, we will discuss advantages and disadvantages of these two analysis approaches and the output data they provide. XPS reference data from the bacterial strain are provided, and we propose that planktonic cells of this strain (DSM 50090) to be used as a reference material for surface chemical analysis of such bacterial systems.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+AS+SE+SS-TuM

Progress and Challenges in Industrial Applications

Moderators: Alex Tselev, University of Aveiro, Portugal, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SE+SS-TuM-1 Progress on Commercializing Doped Diamond Materials and Devices**, ***Anna Zaniewski,*** Advent Diamond **INVITED**

Diamond has long been recognized as a potentially transformative material for power, sensor, and quantum applications. However, realizing the potential of diamond has depended upon a series of breakthroughs in the growth, design, and fabrication of diamond for electronics. Most notably, CVD growth of doped diamond has been a catalyzing breakthrough for realizing next-generation diamond components. Advent Diamond will present progress on achieving commercialization of diamond components and outline future targets for semiconducting and quantum devices.

8:40am **CA+AS+SE+SS-TuM-3 Advanced in Situ Transmission Electron Microscopy: A Powerful Tool for Materials Science, Catalysis, Energy Storage & Lifescience Applications**, ***Hugo Pérez-Garza,*** DENSsolutions, Netherlands **INVITED**

We introduce our technology for in situ studies inside transmission electron microscope (TEM), where next to heating and biasing studies, also environmental studies (i.e. in gaseous or liquid environments) are made possible. The systems rely on a Micro Electro-Mechanical System (MEMS)-based device as a smart sample carrier, which contains an integrated set of biasing electrodes or an integrated microheater, to enable in situ electrochemistry, catalytic studies, failure analysis and biomedical studies, among others. As a result, the system provides users with the capability to visualize exciting dynamics in vacuum or liquid/gas environments as a function of different stimuli. In order to provide meaningful results and address historical challenges, our MEMS device controls the flow direction and ensures the gas/liquid will always pass through the region of interest. Thereby, the developed systems offer the opportunity to define the mass transport and control the kinetics of the reaction. Furthermore, the systems allow to control the liquid thickness, enabling resolutions that can go even down to 2.15 Å (for a 100nm liquid thickness). We believe that our developments will play a fundamental role in addressing many of the research questions within battery optimization, fuel cells, (electro)catalysis, as well as for advanced (bio)materials and nanomedicine. Furthermore, it will the unique possibility to visualize biological processes in real time, without the need of vitrifying the biological specimen.

Keywords: Transmission electron microscopy, in situ, MEMS, environmental studies, stimuli

9:20am **CA+AS+SE+SS-TuM-5 Chemical Analysis Using Laboratory-Based Hard X-Ray Photoelectron Spectroscopy: The Binding Energy Reference Challenge**, *A. Vanleenhove, F. Mascarenhas,* ***Thierry Conard,*** IMEC, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces and is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

This new in-lab technology however comes with new challenges. By the increase of effects which were less pronounced or did not play a role in the analysis with soft X-ray photoelectron spectroscopy the exact binding energy determination and hence analysis of chemical bonding inside layers and at interfaces is more challenging. The recoil effect for instance, which is related to preservation of momentum, resulted in electron energy shifts well within the error bar of peak position determination for XPS spectra. For HAXPES, the recoil effect has to be taken into account, especially when examining low Z materials. Charging effects play a bigger role as well. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from

HAXPES analysis. Vertical charge build up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in ‘simple’ non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises complex oxide layers with varying thickness on Si samples and metal/high-k/Si stacks including high-k materials as HfO_2. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the *HAXPES Lab* instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

11:00am **CA+AS+SE+SS-TuM-10 Integrating Spatial Multiomics Using Giant Cluster Imaging Mass Spectrometry at the Single-Cell Level**, ***Hua Tian,*** University of Pittsburgh **INVITED**

Tissue is highly organized with diverse cells that interact and communicate. Together with numerous biomolecules (e.g. metabolites and lipids) of cellular processes, the multilevel heterogeneities drive the biological function and disease-associated discoordination[1-2]. This spatial complexity is often ignored by traditional tissue assay. Mass spectrometry imaging holds the potential to visualize the heterogeneous cell organization and biomolecules in their context. However, it is challenging to achieve high spatial resolution and high chemical sensitivity toward different biomolecules. Moreover, the correlation of spatial omics in a single sample is impossible due to the difficulty of preserving the fast-changing metabolites.

To overcome these analytical hurdles, innovative technology and methodology are developed for omics imaging in single cells. On the same frozen-hydrated tissue, successive $(H_2O)_{n\ (n>28k)}$-GCIB-SIMS and C_{60}-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 µm resolution. The novel ion source, $(H_2O)_{n(n>28k)}$-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to *m/z* 6000 [3-12]. Coupled with cryogenic analysis, the tissue is analyzed at near nature state, retaining the spatiotemporal distribution of metabolites and lipids. The AI-aided computational processing is used to register the omics in different cell types for further discriminant analysis.

With the new development, a number of tissues are imaged. On breast cancer tissue, the high population of macrophages (CD68) and less infiltration of immune cells (CD45, CD4) are observed, as well as the variation of the metabolic state in different cells. Several phosphatidylinositol species are concentrated in the epithelial tumor cells (pan-cytokeratin), along with desaturated lipids and GSH, indicating the mechanism of immune resistance and antioxidation for tumor survival [27]. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue[37]. On liver tissue, distinct lipid clusters colocalize with periportal and pericentral proteins, and metabolic and lipidomic signature varies in distinct liver cells (*e.g.,* sinusoidal, Kupffer, hepatocytes, Ito stellate, immune cells). Similar to protein markers, further clustering analysis shows that metabolites and lipids classify the cell types for the first time. The multimodal SIMS imaging opens broad applications for exploring various biological phenomena of cellular/biomolecular interactions in health/disease.

11:40am **CA+AS+SE+SS-TuM-12 Atom Probe Tomography Using Wavelength-Tunable, Femtosecond-Pulsed Coherent Extreme Ultraviolet Radiation**, ***Ann Chiaramonti,*** *B. Caplins, J. Garcia, L. Miaja-Avila, N. Sanford,* National Institute of Standards and Technology (NIST) **INVITED**

Laser-pulsed atom probe tomography (LAPT) is a powerful tool for materials characterization due to its desirable combination of high spatial resolution and analytical sensitivity. In state-of-the-art LAPT, the thermal pulse resulting from a near-ultraviolet (NUV) laser (E=3.5 eV to 3.6 eV; λ=355 nm to 343 nm) incident on the sample provides the energy to overcome the activation barrier for field ion evaporation.LAPT has been used successfully to characterize a wide range of materials including metals, semiconductors, insulators, biological materials, and even liquids. However, the thermal process is not without drawbacks. LAPT data quality can be degraded due to for example: thermal tails that limit sensitivity; the formation of cluster ions that may have isobaric overlap with elemental species; undetected neutral species which can adversely influence composition measurements; and unresolvable multiple hits which result in a loss of information. Data loss due to multiple hits and neutral species is particularly problematic for many ionic and covalent materials; it can limit the recovery of bulk stoichiometry or composition to a narrow range of experimental conditions, if at all [1,2].

Ionizing radiation in the extreme ultraviolet (EUV) region of the electromagnetic spectrum (E=10 eV to 100 eV; λ=124 nm to 12 nm) offers potential new field ionization pathways (e.g. direct photoionization and Auger decay) for atom probe tomography.Much of the EUV photon energy band is above the work function and ionization potential of any naturally occurring element, and photoionization cross-sections peak in the EUV band across the entire periodic table [3]. EUV is also highly absorbed within only the first few nm of the sample surface.

Instrument design and results from the world’s first EUV radiation-pulsed atom probe microscope are presented. This instrument uses tunable wavelength (photon energy) femtosecond-pulsed coherent EUV radiation from phase-matched high harmonic generation in a hollow waveguide. Initial experiments demonstrate successful EUV (E=41.85 eV; λ=29.6 nm) radiation-pulsed field ion emission in a variety of materials systems. Time-independent background levels, delayed evaporation tails, peak widths, charge state ratios, multiple hit counts, and the relative number of cluster ions will be compared to NUV LAPT experiments on the same samples and specimens.

[1] Mancini, L. *et al*. J. *Phys. Chem. C***118** (2014) 24136.

[2] Diercks, D.R. *et al. J. Appl. Phys.***114** (2013) 184903.

[3] Yeh, J.-J. and I. Landau. *At. Data Nucl. Data Tables***32** (1985) 1.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL+AS+EM-TuM

Optical Characterization of Thin Films and Nanostructures

Moderators: Tino Hofmann, University of North Carolina at Charlotte, **Mathias Schubert**, University of Nebraska - Lincoln

8:00am **EL+AS+EM-TuM-1 Femtosecond Time Resolved Pump-Probe Spectroscopic Ellipsometry – Applications and Challenges**, ***Rüdiger Schmidt-Grund,*** TU Ilmenau, Germany **INVITED**

I will introduce the method fs-time resolved pump-probe spectroscopic ellipsometry (TSE), recently developed by us [1], as a mighty instrument to investigate the electronic structure and lattice properties of materials in great detail, going beyond many established experimental methods. TSE measures the transient complex dielectric function after optical excitation of charge carriers, which gives us a powerful tool to probe band structure, joint-density of states and transition matrix elements in various regions of the Brillouin zone as well as dynamic phenomena like carrier-carrier scattering, carrier-phonon scattering, excitation, and relaxation. As all this properties and effects in general also depend on the transient carrier density, analysis of TSE data provides vast knowledge about the electronic structure dynamics of materials, in particular valuable for fundamental theory approaches.

After excitation with an intense pump-laser, electrons and holes are created in the conduction and valence bands, respectively. These excited carriers then can scatter within the Brillion zone and interact with the lattice. This leads to dynamic carrier distribution changes in energy and momentum within time scales of fs up to ns or longer. The ellipsometry probe pulse then feels the actual energetic charge carrier distribution at a given delay time step, as expressed in changes of the dielectric function due to Pauli blocking or enabling of new transitions, energy shifts, as well as Drude response induced by these excess carriers in the respective band states. When modelling the experimentally found transient dielectric function with appropriate line shape model functions under mutual comparison with theoretically obtained data for the band structure and joint density of states, we can identify the positions of the charge carriers within the band structure in time, energy, and momentum.

Modelling TSE data is a very complex task: The spatial distribution of the excited carriers must be considered in transfer-matrix analysis, many time-delay steps have to be analysed simultaneously in model function approximation to identify positive and negative contributions as well as to obtain physically meaningful time-evolution of the parameters, and many more challenges. To circumvent the problems, we apply machine-learning based algorithm to find the best modelling of the data.

In my presentation I will introduce technical details of the method TSE, discuss modelling strategies, and give examples of processes observed in various material systems.

[1] S. Richter, M. Rebarz, O. Herrfurth, S. Espinoza, R. Schmidt-Grund, and J. Andreasson, Rev. Sci. Instrum. 92, 033104 (2021)

8:40am **EL+AS+EM-TuM-3 Evolution of Anisotropy and Order of Band-to-Band Transitions, Excitons, Phonons, Static and High Frequency Dielectric Constants Including Strain Dependencies in Alpha and Beta Phase ($(Al_xGa_{1-x})_2O_3$,** ***Megan Stokey****, R. Korlacki, M. Hilfiker, T. Gramer, J. Knudtson,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight,* Linkoping University, Sweden*; A. Mock,* Weber State University*; A. Mauze, Y. Zhang, J. Speck,* University of California Santa Barbara*; R. Jinno, Y. Cho, H. Xing, D. Jena,* Cornell University*; E. Ahmadi,* University of Michigan*; V. Darakchieva,* Lund University, Sweden*; M. Schubert,* University of Nebraska-Lincoln

The rhombohedral alpha and monoclinic beta phases of gallium oxide both make promising candidates for ultra-wide bandgap semiconductor technology. Of particular interest are alloyed films and the evolution of anisotropic optical properties with respect to both alloy composition and strain induced effects. Here, we study alpha and beta phase $(Al_xGa_{1-x})_2O_3$ via a combined density functional theory and generalized spectroscopic ellipsometry approach across a range of alloying. Infrared-active phonon properties, static dielectric constants and midband gap indices of refraction are quantified.[1,2,3] Strain and alloying effects are shown and compared to previous theoretical works.[4] Bandgaps, excitons, and high-frequency dielectric constants are also investigated in the visible to vacuum-ultra-violet (VUV) spectral range.[5,6,7,8] We identify a switch in band order where the lowest band-to-band transition occurs with polarization along the ordinary plane in α-Ga--$_2$O-$_3$ whereas for α-Al-$_2$O$_3$ the lowest transition occurs with polarization in the extraordinary direction. With this, we present the most comprehensive picture of optical properties' evolution along composition and strain currently available.

[1] M. Stokey, R. Korlacki, *et al.,* Phys. Rev. Materials 6, 014601 (2022)

[2] M. Stokey, T. Gramer, *et al.,* Appl. Phys. Lett. 120, 112202 (2022)

[3] M. Stokey, R. Korlacki, *et al.*, "The influence of strain and composition on the infrared active phonons in epitaxial β-(AlxGa1-x)2O3 deposited onto (010) β-Ga2O3", *In Preparation*

[4] R. Korlacki, M. Stokey, A. Mock, *et al*., Rev. B 102, 180101(R) (2020)

[5] M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. 118, 062103 (2021)

[6]M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. XX, XX (2022)

[7] M. Hilfiker, U. Kilic, M. Stokey, *et al.,* Appl. Phys. Lett. 119, 092103 (2021)

[8] M. Hilfiker, U. Kilic, *et al.,* Phys. Lett. 114, 231901 (2019)

9:00am **EL+AS+EM-TuM-4 Engineering the Bi-Signate Broadband Enhanced Chirality Revealed by All Dielectric *Nanoboomerang* Structure***,* ***Ufuk Kilic****, M. Hilfiker, A. Ruder, S. Wimer, S. G. Kilic, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

Chirality phenomenon has recently aroused remarkable interest because of its promising potential applications in optics, catalysis and sensing. However, the large-scale mismatch between the wavelength of incident circular polarized (chiral) light and the size of natural chiral crystals (such as quartz or benzyl) or small size of chiral molecules (such as DNA or proteins) led the chiral light-matter interactions to be extremely weak in nature and cannot be made tunable [1]. The recent studies showed that one can obtain strong and tunable chiral response using subwavelength scale structures so-called metamaterials. As a promising large-scale area, bottom-up 3D nanomorphology fabrication method with precise sample stage manipulation ability, the glancing angle deposition (GLAD), is envisioned as a promising route to the experimental realization of strong and tunable chiroptical responses [1].

Here, we propose a simplistic chiral-nano-platform: all-dielectric spatially coherent, superlattice type, distorted L-shape metamaterials so-called chiral *nanoboomerangs* which were fabricated using custom-built, ultra-high-vacuum electron beam evaporated GLAD instrument. The structure consists of two achiral silicon nano-columnar segments, but the sample stage is rotated prior to the fabrication of second segment. Using a Mueller matrix spectroscopic ellipsometry based chiroptical characterization method, we found that our proposed large-scale nanophotonic metamaterial platform exhibits extremely broadband, large, tunable, and bi-signate chiroptical response within the near infrared to vacuum ultraviolet spectral range. We believe that this new material platform is a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems, and chiral-topological insulators.

Reference:

1. Kilic, U. *et al.*, Advanced Functional Materials, 31(20), 2010329, (2021).

9:20am **EL+AS+EM-TuM-5 Structural Properties and Optical Constants of CaF_2 at 300 K from 0.03 to 6.5 eV***,* ***Jaden R. Love****, N. Samarasingha, C. Armenta, S. Zollner,* New Mexico State University*; H. Kim,* National Institute of Aerospace (NIA)

In this undergraduate student presentation, we describe the structural and optical properties of calcium fluoride (CaF_2) an insulator with an ultrawide band gap of 12 eV and a large exciton binding energy of 1 eV. CaF_2 has a wide range of transparency from 125 meV in the infrared to 10 eV in the ultraviolet making it an ideal substrate for optical devices. Such optical devices include actively tunable transmission filters utilizing certain phase change memory materials (PCM's) which can be used for higher resolution imaging on satellites. Most studies of the optical constants of CaF_2 were performed in the 1960's and are discussed in [1]. Revisiting these optical constants using modern ellipsometry equipment and specimens from different manufacturers with (100) and (111) orientation seems timely. CaF_2 crystallizes in the fluorite structure with space group Fm-3m and has a lattice constant of 5.4626 Å. The Ca-$^{2+}$ atoms are located in the Wyckoff (4a) position at the origin. The F$^-$ atoms are at the (8c) positions (¼,¼,¼) and (¼,¼,3/4). There is a three-fold degenerate Raman-active T_{2g} mode and a three-fold degenerate infrared active T_{2u} mode, which splits into a transverse optical (TO) doublet and a longitudinal optical (LO) singlet. The T_{2u} mode can be observed with Fourier-transform infrared ellipsometry and described with a Lorentzian. The TO and LO energies are 261 and 477 cm^{1-}, respectively, with an amplitude A=4.1, a broadening of 4 cm^{1-}, and a high-frequency dielectric constant of 1.98[1]. A dip in the reststrahlen band is due to two-phonon absorption described with an anharmonically broadened Lorentzian. In the visible and near ultraviolet approaching 6.5 eV, normal dispersion can be described with a pole located at 7.48 eV and a Tauc-Lorentz oscillator at 20 eV. The imaginary part of the pseudo dielectric function, $<\varepsilon_2>$ is negative above 3 eV. This indicates a surface layer of 2 to 5 nm thickness with a larger refractive index than that of the bulk substrate. We apply the CaF_2 optical constants to determine the thickness of an SiO_2 layer on the CaF_2 substrate.

[1] D. F. Bezuidenhout in Handbook of Optical Constants of Solids II, edited by E. D. Palik

(Academic, San Diego, 1998).

9:40am **EL+AS+EM-TuM-6 Optical Dielectric Function of a Solution-Processable Thiazolothiazole Thin Films Determined by Spectroscopic Ellipsometry***,* ***Nuren Shuchi****, J. Mower, V. Stinson, M. McLamb, G. Boreman, M. Walter, T. Hofmann,* University of North Carolina at Charlotte

Fluorescent molecules are ubiquitous in contemporary technologies and can be found for instance in energy-conversion devices [1], sensors [2], and are used for biological imaging techniques [3]. Recently, families of fluorescent molecules which combine multiple functionalities have gained considerable attention [4]. Significant progress has been made in the field of molecular electronics due to the advent of unique oligothiophenes [5] and thiadiazolobithienyl dyes [6]. We have synthesized solution-processable, 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole (TTz) dyes for thin film organic electronics applications. The TTz dyes were synthesized by refluxing 4-pyridinecarboxaldehyde, 4-(dibutylamino)benzaldehyde, and dithiooxamide in 40 mL of anhydrous dimethylformamide for 6 hours at 120 °C. The reaction solution was chilled overnight and crude precipitate was collected using vacuum filtration and rinsed with dimethyl sulfoxide and water. The isolated product was purified using silica gel column chromatography (Silica Flash M60) with a 1:1 hexanes/chloroform mixture. <1,0,0> Si wafers were cut to approximately 20 mm x 15 mm and sonicated in acetone, deionized water, and isopropyl alcohol for 15 minutes. The wafers were dried with compressed nitrogen gas and treated with UV / ozone for 15 minutes. The Si wafers and a 16.1 g/L 1,2-dichlorobenzene solution of the thiazolothiazole dye were heated to 55 °C in a nitrogen glove box. While in the glove box, 90 µL of the TTz solution was spin coated onto each Si wafer at 2000 RPM for 30 seconds. The wafers were heated to 110 °C for 20 minutes and stored in the glove box away from light. In this presentation, we will discuss spectroscopic ellipsometry data obtained from a 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole thin films deposited by spin coating on a silicon substrate in the spectral range from 354 nm to 1907 nm. The ellipsometric data were analyzed using a stratified layer model composed of thiazolothiazole thin film, native SiO_2 oxide, and Si substrate. The model dielectric function of the thiazolothiazole thin film was composed of a series of Tauc-Lorentz and Gaussian oscillators. The best-model calculated data are rendering the experimental data very well. Obtained transition energies will be reported and compared with those of related thiazolothiazole dyes. **References:** [1] J. Am. Chem. Soc. **133**, 20009 (2011). [2] Chem. Soc. Rev. **40**, 2222 (2011). [3] BMC Systems Biology **2**, 1(2008). [4] CHEM-EUR J. **19**, 2582 (2013). [5] J. Phys. Chem. Lett. **9**, 1958 (2018). [6] Sci. Rep. 6, 18870 (2016).

11:00am **EL+AS+EM-TuM-10 Bandgap Engineering of Polycrystalline Ge-doped Sb_2Se_3 Thin-Film: Surface and Optical Properties*, Sanghyun (Philip) Lee,*** University of Kentucky*; M. McInenery,* Rose-Hulman Institute of Technology

Antimony Chalcogenide, $Sb_2(S_x,Se_{1-x})_3$ is a third-generation thin-film photovoltaic device. $Sb_2(S_x,Se_{1-x})_3$ solar cells have received growing attention due to their favored properties with <9.2 % efficiency. In particular, $Sb_2(S,Se)_3$ has a high absorption coefficient at visible light (>10^5 cm^{-1}), tunable bandgap (1.0 eV – 1.7 eV), stable upon exposure to sunlight under ambient conditions.

For the optimization of bandgap of Sb_2Se_3 alloy films, Ge-doped Sb_2Se_3 thin-film for solar cells applications have been studied with various compositions and doping concentrations, showing different crystallization, surface, and optical characteristics. Sb_2Se_3 thin-films are crystalline as deposited and on heating with orthorhombic structures. As a few molar percent of Ge doped into Sb_2Se_3 (<15 %) films (GeSbSe), polycrystalline films are formed upon annealing above 200 - 250 C, demonstrating no significant dependence of lattice constant on the Ge doping level. However, most GeSbSe studies are focused on amorphous Sb_2Se_3 films doped with higher Ge concentration (> 15 %).

In this contribution, we have fabricated and studied the bandgap energy and surface properties of polycrystalline GeSbSe thin-films (<15 %) for the application to the photovoltaic absorber. We investigated critical optical properties of absorption coefficient and engineered optical bandgap of films grown at different temperatures. Optical responses are explored with UV-Vis spectrometer. Moreover, scanning electron microscopy and Energy-dispersive X-ray spectroscopy are used to confirm optical bandgap, surface structures, and chemical composition of GeSbSe thin-films grown by Vapor Transport Deposition at different film growth temperatures. The optimum optical characteristics of thin-film absorber materials depend on film surface microstructure, which in turn affects the overall optical behaviors of GeSbSe films.

Ge-doped Sb_2Se_3 thin-films (<15 %) are polycrystalline with thickness around 1 um grown at 500 C and 520 C. As the deposition temperature increases from 500 C to 520 C, uniform grains of approximately 0.9 um at 500 C become mixed grains of larger (~6 um) and smaller grains (~0.9 um), revealed by Scanning Electron Microscopy characterization. The surface morphology becomes smooth (500 C) to irregularly rougher (520 C). For the characterization of optical properties, the absorption coefficient is >10^5/cm near 600 nm for both films. Based on the widely used Tauc's relation, the optical bandgap of Ge-doped Sb_2Se_3 thin-film absorbers is extracted as 1.15 eV and 1.23 eV for samples grown at 500 C and 520 C, respectively.

11:20am **EL+AS+EM-TuM-11 Optical Properties of Orthorhombic LiGa0$_2$ from Far-Infrared to Vacuum Ultraviolet*, Teresa Gramer,*** *E. Williams, M. Stokey, R. Korlacki, U. Kilic, M. Hilfiker, M. Schubert,* University of Nebraska - Lincoln

Within the Li_2O-Ga_2O_3 oxide system, $LiGaO_2$ (LGO) and multiple phases of Ga_2O_3 (GO) are prospective ultra-wide bandgap metal oxides for electronic and optoelectronic applications [1]. While both GO and LGO have recently been identified to most likely trap holes and which makes achievement of sufficient p-type conductivity difficult [2], LGO is particularly promising as a substrate for heteroepitaxial growth of GaN due to very small lattice mismatch (<1%), and a composite LGO/β-GO substrate has also been demonstrated [3]. Here, we provide a comprehensive study of the fundamental optical and phonon mode properties of high-quality single-crystals of LGO using generalized spectroscopic ellipsometry in combination with hybrid-level density functional theory calculations that covers the optical properties in the far-infrared to vacuum ultraviolet spectral range. In the mid- to far-infrared range, we identify all 33 infrared-active pairs of transverse and longitudinal optical phonon modes. We derive the anisotropic mid-band gap indices of refraction and static dielectric constants. In the visible to vacuum ultraviolet spectral range we identify band-to-band transitions and discuss near band-gap excitonic contributions. We compare the obtained results with the previous experimental and theoretical studies. [4,5,6]

[1] A review of band structure and material properties of transparent conducting and semiconducting oxides: Ga$_2$O3 , Al$_2$O3 , In$_2$O3 , ZnO, SnO_2, CdO, NiO, CuO, and Sc$_2$O3 , Joseph A. Spencer, Alyssa L. Mock, Alan G. Jacobs, Mathias Schubert, Yuhao Zhang, and Marko J. Tadjer , Applied Physics Reviews 9, 011315 (2022)

[2] Self-trapped holes and polaronic acceptors in ultrawide-bandgap oxides, John L. Lyons, Journal of Applied Physics 131, 025701 (2022)

[3] Composite substrate $LiGaO_2$ (0 0 1) β-Ga$_2$O3 (1 0 0) fabricated by vapor transport equilibration, Zhang, Jungang & Xia, Changtai & Li, Shuzhi & Xu, Xiaodong & Wu, Feng & Pei, Guangqing & Xu, Jun & Zhou, Shengming & Deng, Qun & Xu, Wusheng & Shi, Hongsheng. Mater. Lett. 60. 3073-3075. (2006)

[4] Optical properties of lithium gallium oxide, S. Tumenas, P. Mackonis, R. Nedzinskas, L. Trinkler, B. Berzina, V. Korsaks, L. Changc, M.M.C. Chou , Applied Surface Science, Volume 421, Part B. (2017)

[5] Quasiparticle self-consistent GW band structures and high-pressure phase transitions of $LiGaO_2$ and $NaGaO_2$, Santosh Kumar Radha, Amol Ratnaparkhe, and Walter R. L. Lambrecht, Physical Review B 103, 045201 (2021)

[6] Piezoelectric, Elastic and Dielectric Properties of $LiGaO_2$, Satoshi Nanamatsu et al, Jpn. J. Appl. Phys. 11 816 (1972)

11:40am **EL+AS+EM-TuM-12 Optical and X-ray Characterization of Ge-Sn Alloys on GaAs*, Haley Woolf,*** *C. Emminger, C. Armenta,* New Mexico State University*; M. Kim,* QuantTera*; S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe the optical and x-ray characterization of a thick $Ge_{1-y}Sn_y$ alloy grown on GaAs by chemical vapor deposition. From (224) x-ray reciprocal space maps we find that the alloy layer is grown pseudomorphically on the GaAs substrate. Therefore, we can use (004) rocking curves and reciprocal space maps to determine the alloy composition based on Vegard's Law. We find y=0.012.

For ellipsometry measurements, we first cleaned the surface ultrasonically with water and isopropanol to remove adsorbed organic overlayers and a portion of the native oxide. The remaining native oxide was found to be 2.6 nm thick. We then acquired the ellipsometric angles ψ and Δ from 0.5 to 6.5 eV photon energy and 60 to 75° incidence angle using a vertical variable angle of incidence ellipsometer (VASE) equipped with a computer-controlled Berek wave plate compensator. Due to the low tin content, these ellipsometric angles and the resulting pseudo-dielectric function could be described very well using a four-layer model, consisting of a GaAs substrate, a pure Ge layer, GeO_2 oxide, and air as the ambient. This results in an epilayer thickness of 1600 nm.

After fixing the thickness, we also obtained the dielectric function ε of the epitaxial $Ge_{1-y}Sn_y$ layer from a point-by-point fit. This is very similar to that of bulk Ge. The second derivative $d^2\varepsilon/dE^2$ was fitted with analytical line shapes to determine the critical point parameters of the alloy (amplitude, energy, broadening, and phase angle). The energy was compared with predictions from continuum elasticity theory based on established deformation potentials for Ge.

12:00pm **EL+AS+EM-TuM-13 Zinc Gallate ($ZnGa_2O_4$) Epitaxial Thin Films: Determination of Optical Properties and Bandgap Estimation Using Spectroscopic Ellipsometry***, S. Bairagi, J. Chang, C. Hsiao, R. Magnusson, J. Birch,* Linköping University, Sweden*;* ***Jinn P Chu,*** National Taiwan University of Science and Technology, Taiwan*; F. Tarntair,* National Yang Ming Chiao Tung University, Taiwan*; R. Horng,* National Yang Ming Chiao Tung University, Taiwan*; K. Järrendahl,* Linköping University, Sweden

Very high quality Zinc gallate (ZGO) epitaxial thin films were grown on c-plane sapphire substrates by Metal-Organic Chemical Vapor Deposition and investigated using Spectroscopic Ellipsometry (SE). Two or more samples were grown with identical growth conditions but different growth times to obtain samples with similar crystallographic and optical properties but different thicknesses. Their thickness, roughness and optical properties were then determined using a Multiple Sample Analysis (MSA) based approach in tandem by the regression analysis of the optical model and measured data for all samples. Another set of ZGO samples were grown for the same growth time but etched using ion-bombardment for different time durations to achieve different thicknesses. These samples were also analyzed by SE using MSA and it was observed that etching times of 1 – 4 minutes had no discernible impact on the material's optical properties. It was also observed that both sets of samples exhibited identical optical properties and thus could be described using the same optical model, thereby showcasing the robustness of the MSA model. Line shape analysis of resulting absorption coefficient dispersion revealed that ZGO exhibited both direct and indirect interband transitions. A modified Cody formalism was employed to determine their optical bandgaps, resulting in a direct bandgap of 5.07 ± 0.015 eV and indirect bandgap of 4.72 ± 0.015 eV. These values were compared to values obtained using other popular bandgap extrapolation procedures to find which technique resulted in the most linear line shape. In a subsequent study, the first set of samples was annealed to different temperatures and their optical properties were analyzed using SE. It was observed that the onset of absorption and hence the optical bandgap blue-shifted to higher photon energies as the annealing temperature was increased from 800° C to 1100° C. This was a consequence of inter-diffusion between the ZGO thin film and sapphire substrate, resulting in the formation of an epitaxial β-(Al, Ga)O intermediate layer between the two, and modification of ZGO to Zn(Al, Ga)O due to diffusion of Al. Post analysis it was observed that the formation of β-(Al, Ga)O intermediate layer began already at 800° C and led to an increase in the overall film thickness with increasing annealing temperatures. The direct and indirect optical bandgaps for the Zn(Al, Ga)O thin film were determined to be 5.10, 5.19, 5.73 eV and 4.80, 4.87, 5.45 eV for 800, 950 and 1100° C, respectively and the increase is attributed to the diffusion of Al from the sapphire substrate.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-TuM

Energetic Processes and Tailored Surfaces in Heterogeneous Catalysis

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, Germany, **Arthur Utz**, Tufts University

8:40am **HC+AS+SS-TuM-3 Adsorption and Reaction of Acetic Acid on Single-Crystal and Faceted Nanoparticle Anatase TiO$_2$(101) Surfaces***, C. O'Connor, R. Ma, Y. Wu, W. DeBenedetti, F. Gao, Y. Wang, G. Kimmel,* ***Zdenek Dohnálek,*** Pacific Northwest National Laboratory

Understanding the adsorption and reactivity of carboxylic acids on anatase TiO$_2$ is of great interest in catalysis for the potential synthesis of selective carbon-coupling reaction products. A comparative investigation of the adsorption and reaction of acetic acid on single-crystal planar and faceted nanoparticle anatase TiO$_2$(101) surfaces was performed using a combination of infrared spectroscopy, temperature-programmed reaction spectroscopy and scanning tunneling microscopy. Acetic acid adsorbs as bidentate acetate and monodentate acetic acid dependent on the adsorption temperature as determined by infrared spectroscopy and scanning tunnelling microscopy measurements on single-crystal TiO$_2$ under ultra-high vacuum conditions. The adsorption of bidentate acetate has a saturation coverage of 0.5 ML. However, high-density phases containing a mixture of bidentate acetate and monodentate acetic acid and solely monodentate acetic acid occur at low temperature conditions. The sole presence of bidentate acetate is observed at elevated temperature due to the facile conversion of monodentate acetic acid to bidentate acetate and desorption of monodentate acetic acid which precludes investigating the reactivity of high-density phases under vacuum conditions. The presence of monodentate acetic acid persists to notably higher temperatures on the faceted nanoparticles than single-crystal TiO$_2$. The reaction of bidentate acetate produces ketene and water as determined by temperature-programmed reaction spectroscopy on single-crystal TiO$_2$. Notably, there is an absence of carbon-carbon coupled products, such as acetone, from the sole reaction of bidentate acetate. The selectivity of bidentate acetate is independent of coverage up to the saturation coverage. Similarly, the reaction of acetic acid on faceted nanoparticle TiO$_2$ produces predominantly ketene and water as determined by temperature-programmed reaction spectroscopy under low vacuum conditions. This study provides mechanistic insight into the reactivity and stability of surface-bound intermediates that are present for the reaction of acetic acid on anatase TiO$_2$ catalysts.

9:00am **HC+AS+SS-TuM-4 Phase Transformation of Single Micro-Sized TiO$_2$ Crystals***, W. Lu, H. Zhu, N. Craft, K. Park,* ***Zhenrong Zhang,*** Baylor University

Understanding the reactivity of various crystal faces in different polymorphs of TiO$_2$ in photoreaction is important for many photocatalytic applications. Here, we monitored and studied the anatase-rutile phase transition (ART) processes of individual micro-sized TiO$_2$ crystals from the pure anatase phase to the mixed-phase, then to the rutile phase. High-quality micro-sized anatase TiO$_2$ crystals with a large percentage of (001) facets were hydrothermally synthesized. Micro-Raman spectroscopy mapping and scanning electron microscope (SEM) images were obtained at different annealing stages to correlate the crystal structure transformation with the morphology change. The ART processes of individual anatase particles are distinctive and depend on the various defects which serve as rutile nucleation sites. Two types of transition pathways are observed. In one type of growth pathway, rutile nucleation was formed at a corner of an anatase crystal. The rutile phase then gradually propagated over the rest part of the microparticle. The phase concentration calculated from Raman spectra revealed that the ART transition follows the first-order reaction mechanism. In the other type of growth pathway, multiple rutile nucleation sites formed simultaneously on different edges and corners of the microcrystal. The rutile phase then spreads over the whole crystal from these nucleation sites forming multi-grain crystals.

9:20am **HC+AS+SS-TuM-5 Reactivity of Formic Acid on Single Atom Rh Supported on Fe$_3$O$_4$(001)***,* ***Christopher Lee****, M. Sharp, S. Smith, B. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysis is a growing area of research due to the potential to qualitatively transform the activity and selectivity of supported metal catalysts. However, the fundamental surface science studies of their unique properties have not been widely studied. Here we investigate the reactivity of formic acid on several model Rh catalysts, including single Rh adatoms, Rh incorporated into the support oxide lattice, and metallic Rh clusters on Fe$_3$O$_4$(001) under ultrahigh vacuum conditions. The single Rh adatoms are found to be the most active towards CO$_2$ production, followed by incorporated Rh and then by Rh nanoclusters. While the reaction of formic acid with Fe$_3$O$_4$(001) primarily results in CO desorption at ~570 K, the addition of small amounts of single adatom Rh (~0.01 Rh per Fe$_3$O$_4$(001) unit cell (u.c.)) results in a dramatic shift towards CO$_2$ production at lower temperatures starting at 540 K and dropping to ~470 K at larger HCOOH coverages. The incorporated Rh system also yields CO$_2$ product, but it takes ~15-20 times as much Rh to achieve the same activity as the Rh adatoms. Rh nanoclusters exhibit reactivity similar to metallic Rh with low-temperature CO$_2$ and H$_2$ desorption at ~310 K while still producing substantial amounts of CO$_2$ at 450-500 K, not observed on pure Fe$_3$O$_4$(001). These differences demonstrate that different forms of Rh supported on Fe$_3$O$_4$(001) affect the reactivity of the catalytic surface beyond the local stabilized transition metal site. The stabilized adatoms turn over multiple adsorbates to products demonstrating the importance of spillover from the support oxide. Furthermore, the single Rh adatoms and incorporated Rh exhibit an intermediate activity distinct from metallic Rh nanoparticles or the Fe$_3$O$_4$(001) substrate, demonstrating the additional degree of reactive tuning provided by single-atom catalysts. The similarity in reactive behavior between the Rh adatom and mixed Rh oxide systems hints toward a common mechanism between the systems. The much larger reactivity of the Rh adatom system suggests that under reaction conditions, a small amount of the mixed Rh oxide may be dynamically converted to Rh adatom and that the Rh adatom is responsible for the lower temperature CO$_2$ activity.

9:40am **HC+AS+SS-TuM-6 WO$_3$/Ag$_2$S type-II Hierarchical Heterojunction for Improved Charge Carrier Separation and Photoelectrochemical Water Splitting Performance***,* ***Jyoti Yadav****, J. Singh,* IIT DELHI, India

In the present work, WO$_3$/Ag$_2$S heterojunction was fabricated to achieve an improved photoelectrochemical (PEC) water splitting performance. To prepare the working electrodes,a two step method was adopted which includes, a thin film of WO$_3$ deposited using DC sputtering and a well-separated Ag$_2$S nanorods fabricated by glancing angle deposition,. The PEC response was studied for bare WO$_3$, Ag$_2$S, and WO$_3$/Ag$_2$S heterojunction. The as-prepared WO$_3$/Ag$_2$S heterojunction samples revealed higher absorption as well as higher photocurrent density of 2.40 mA/cm^2 (at 1V

Ag/AgCl) as compared to bare WO_3 thin film (0.34 mA/cm^2). The enhancement in the photocurrent density of WO_3/Ag_2S electrodes could be ascribed to the formation of the type-II heterojunction between WO_3 and Ag_2S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag_2S nanorods structures results in an effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that WO_3/Ag_2S samples have lower charge transfer resistance at the semiconductor electrolyte interface with high flat band potential. The present work provides a deeper insight on the role of the interface formed between WO_3 and Ag_2S for the photoelectrochemical water splitting response.

11:00am **HC+AS+SS-TuM-10 Using Photon-Stimulated Desorption to Probe the Structure and Reaction Dynamics of Molecules Adsorbed on TiO_2(110)**, ***Greg Kimmel,*** Pacific Northwest National Laboratory **INVITED**

TiO_2 is a widely used photocatalyst. Its ability to oxidize organic contaminants makes it useful, for example, in air and water purification systems and as a thin-film coating for self-cleaning surfaces. As a result of titanium dioxide's practical applications and its potential use in photocatalytic water spitting, it has been the subject of a tremendous amount of research. We have investigated the photon-stimulated reactions of small molecules, such as O_2, CO, and acetone, on rutile TiO_2(110). Experiments on clean, well-characterized single crystal surfaces, including azimuth- and angle-resolved measurements of photo-desorption products, provide key insights into the photochemical reactions of interest. This talk will highlight examples of this approach, including the photochemistry of chemisorbed O_2, the photo-oxidation of CO, and the photon-stimulated reactions of acetone. For the photo-oxidation of CO, the results show that a bridging O-O-C-O intermediate ejects CO_2 perpendicular to the bridging oxygen rows, which is consistent with density functional theory calculations. However, in contrast to earlier suggestions, the reaction kinetics show that the oxidation is a multi-step process. For acetone, the azimuth-resolved measurements of the methyl fragments revealed a second reaction channel that probably involves an enolate intermediate on the surface.

11:40am **HC+AS+SS-TuM-12 Comparison of Pt, Rh and Ir Single Atoms on a Fe_2O_3 Model Support**, ***Gareth Parkinson****, A. Rafsanjani Abbasi, L. Puntscher, F. Kraushofer, P. Sombut, C. Wang,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; M. Eder, J. Pavelec, G. Franceschi, M. Riva, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria

Understanding how the local environment of a "single-atom" catalyst affects stability and reactivity remains a significant challenge. Fe_2O_3 is the most common iron-oxide support material utilized for SAC, but little is known about how metal adatoms bind at its surfaces. In this talk, I will compare and contrast the behavior of Pt, Rh,[1,2] and Ir atoms on the flat, well-ordered (1×1) termination of Fe_2O_3(1-102).[3,4] Using a combination of scanning probe microscopy and spectroscopic data, as well as theoretical calculations, I will demonstrate significant differences between the adsorption site and thermal stability of the metals, as well as differences in their interaction with water and carbon monoxide.

[1] F. Kraushofer *et al.*, Single Atom Catalysts: Surface Reduction State Determines Stabilization and Incorporation of Rh on α-Fe_2O_3(1-102) (Adv. Mater. Interfaces 8/2021). *Advanced Materials Interfaces***8**, 2170045 (2021).

[2] F. Kraushofer *et al.*, Single Rh Adatoms Stabilized on α-$Fe_2O_3(1\bar{1}02)$ by Coadsorbed Water. *ACS Energy Letters***7**, 375-380 (2022).

[3] F. Kraushofer *et al.*, Atomic-Scale Structure of the Hematite α-Fe_2O_3(1-102) "R-Cut" Surface. *J. Phys. Chem. C***122**, 1657-1669 (2018).

[4] G. Franceschi *et al.*, A Model System for Photocatalysis: Ti-Doped α-Fe_2O_3(1-102) Single-Crystalline Films. *Chem. Mater.***32**, 3753-3764 (2020).

12:00pm **HC+AS+SS-TuM-13 HC Graduate Student Finalist Talk: Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe_3O_4(001)**, ***Marcus Sharp,*** PNNL/WSU*; C. Lee, M. Mahapatra, S. Smith, B. Kay, Z. Dohnálek,* PNNL

Single atom catalysts have emerged as a new catalyst frontier due to the need for improved catalyst activity and selectivity. Yet key fundamental challenges exist regarding understanding of how their activity and stability depend on their coordination environment. Surface science studies have the tools necessary to investigate such monodispersed single atom catalysts and their chemistry under well-controlled reaction conditions. Here, we have studied the behavior of Rh on the Fe_3O_4(001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe_3O_4(001) reconstructed surface that has been shown to stabilize single 2-fold coordinated metal adatoms to elevated temperatures. By varying the Rh deposition and annealing temperature, we have identified a series of model catalysts possessing unique Rh sites. These catalysts include Rh adatoms, mixed surface layers with octahedrally-coordinated Rh, small Rh clusters, and large Rh nanoparticles on both mixed and pure Fe_3O_4 surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO_2 adsorption is employed to characterize the chemical and redox properties of these sites. CO binds strongly with Rh adatoms, clusters, and nanoparticles desorbing at higher temperatures but interacts weakly with the Rh-octahedral species. In contrast, CO_2 interacts most weakly with Rh adatoms and nanoparticles, while interactions between Rh-octahedral and Fe-octahedral are indistinguishable. Further, CO_2 is used to distinguish between metallic Rh sites and Fe_3O_4(001) sites, which shows good agreement with our STM results. These model systems allow us to directly investigate reaction mechanisms on different types of catalytic sites furthering our understanding of how to selectively tune catalyst sites for desired reaction pathways. Future studies are directed toward understanding the energetics and reaction pathways of the hydrogenation of unsaturated hydrocarbons and carbonyl functional groups.

Applied Surface Science Division
Room 320 - Session AS+EM+SE-TuA

Surface Analysis Using Complementary Techniques

Moderators: Samantha Rosenberg, Sandia National Laboratory, **Carl A. Ventrice, Jr.**, SUNY Polytechnic Institute

2:20pm **AS+EM+SE-TuA-1 Origins of the Emergent Phenomena at Oxide Interfaces Studied with Complementary X-Ray Spectroscopic and Scattering Techniques***, **Alexander Gray,*** Temple University **INVITED**

Atomic-level design of complex-oxide heterostructures that exhibit functional electronic and magnetic phenomena has become a diverse and vibrant subfield of condensed matter physics and material science. Of particular interest are the material systems wherein rich physics and intricate interplay between various degrees of freedom at the interface give rise to functional properties not observed in the constituent materials. Detection and characterization of these interfacial properties present a unique practical challenge due to the lack of direct yet non-destructive techniques that are capable of probing minute changes in the electronic and magnetic states at a buried interface with element specificity and Ångstrom-level spatial resolution. In this talk, I will discuss several recent studies in which we utilized a combination of complementary x-ray spectroscopic and scattering techniques to understand the origins of the emergent low-dimensional ferromagnetic states in $LaNiO_3/CaMnO_3$ and $CaRuO_3/CaMnO_3$ superlattices. Depth-resolved standing-wave photoemission spectroscopy was used to probe the depth-dependent changes in the electronic states, while soft x-ray resonant magnetic scattering was used to extract the element-specific magnetic profile of the interface. The results of the experiments were compared to and interpreted using state-of-the-art first-principles theoretical calculations.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Award DE-SC0019297.

3:00pm **AS+EM+SE-TuA-3 Multi-Technique Forensic Analysis by Co-Incident XPS & Raman Imaging***, **Robin Simpson**, P. Mack,* Thermo Fisher Scientific, UK

For more than 100 years fingerprint analysis has been ubiquitous in the forensic sciences and is still a core method for identifying individuals in forensics. The techniques used to analyze fingerprints are either structural, for identifying the features of the fingerprints, or chemical, characterizing the composition of the deposited material. Many of these chemical characterization techniques are destructive to the sample preventing any further analysis from being performed or the sample from being preserved as evidence for a later date. Here we show the benefits of using XPS to analyze fingerprints, where the elemental and chemical state composition of a sample can be acquired non-destructively from the top 10 nm of the surface.

In this investigation, we build on our previous work investigating fingerprint analysis. In that study, XPS and XPS mapping techniques were utilized to identify and characterize the contamination of fingerprints. Fingerprints contaminated with TiO-$_2$, and PbO deposited on the silicon wafer can be chemically mapped and visualized using XPS using principal component analysis, PCA.

In this study, we also discuss other examples of forensic analysis including the identification of pharmaceutical substances using complementary XPS and Raman analysis. To achieve this an “over the counter” multi-component analgesic tabletwas crushed to a powder form and deposited onto the substrate. The powder is mapped rapidly using XPS imaging and the data is processed by PCA. This information was used to identify areas for further analysis by high-resolution XPS and Raman. Further Raman analysis was used to characterize the composition of the 3 areas of the sample and identify the compounds contained in them. These are shown to be aspirin, paracetamol, and caffeine through comparison with known sample spectra in the OMINC Raman spectral database.

In the final two examples of forensic analysis workflows in this presentation, we discuss the identification and differentiation between overlapping ink and paint samples deposited on paper or fabric substrates. Raman mapping is used to differentiate between two paint samples that have virtually identical chemistry when analyzed via XPS, and rapid XPS imaging is used to identify the order of events between the deposition of computer-printed ink and handwritten ink from a ballpoint pen.

3:20pm **AS+EM+SE-TuA-4 Comparison of Methods to Quantify Silicone on Hair***, **Michaeleen Pacholski**, B. Johnson, T. Case, T. Powell, D. Carsten, J. Stratton,* The Dow Chemical Company*; C. Ji,* The Dow Chemical Company, China*; M. McIvor, N. Goodman, S. Yusuf, M. Upshur,* The Dow Chemical Company

Silicone has been used as a conditioning agent on hair for a long time.Silicone deposition can produce numerous benefits in reducing the coefficient of friction, improving combability and decreasing frizz.It can be delivered in multiple ways such as conditioning shampoo, rinse off conditioners, leave in conditioners and detangling products.Regardless of how it is delivered to the hair surface, the quantification of silicone on hair is an important metric for R&D product development and marketing.In a large analytical group there are many techniques that can be used including XPS, XRF, ICP, GC and IR.Each has different limits of detection, amount of sample required, time involved to both acquire and analyze the data, etc.A set of samples was generated using both shampoo and rinse off conditioner on both brown and bleached hair for a comparison study.The amount of silicone varied from low to high levels.Comparison of the techniques showed general agreement between all techniques within expectations.These experiments can now guide internal work based on the needs of the specific project and what instrumentation is available within that region.

4:20pm **AS+EM+SE-TuA-7 Progress Towards Atomic Scale Analytical Tomography***, **Brian Gorman**,* Colorado School of Mines*; T. Kelly,* Steam Instruments, Inc*; M. Holtz,* Colorado School of Mines **INVITED**

Atomic-Scale Analytical Tomography (ASAT) has been recently defined as the ability to identify every atom in its place. Specifically, ASAT is the ability to determine the isotopic identity and sub-Angstrom position of 100% of the atoms in a specific volume. Taking this a step further, ASAT should also be able to determine the local electronic structure of these atoms, thus giving rise to true 3-D atomic structure / electronic property relationships. ASAT datasets of semiconductor nanostructures will reveal the 3-D position of individual dopant atoms with pm spatial resolution, the 3-D position of nuclear spin isotopes, nanometer scale changes in strain due to structural defects and lattice mismatch, the 3-D position of point defects such as vacancies, and any electronic band structure changes at all these atomic-scale features.

Undoubtedly, ASAT is a lofty metrology goal but is nearly within reach. Contemporary metrology techniques such as (Scanning) Transmission Electron Microscopy ((S)TEM) are not currently capable of ASAT. (S)TEM can image atomic positions with better than 0.01 nm resolution in some specimens and tilt-series tomographic imaging can give 3-D information, sometimes at atomic resolution. Analytical STEM can be performed at atomic resolution in some cases, although identifying a single atom in 3-D is only possible in limited specimens and with poor depth resolution. Atom Probe Tomography (APT) can provide mass spectral information on individual atoms, however, 3-D image reconstruction methods are constrained by multiple empirical assumptions and lack of information about the specimen that limit the spatial resolution.

Recently, it was demonstrated that correlative TEM and APT on the same specimen can approach ASAT. We used (S)TEM imaging of the specimen before and after APT to define the analyzed 3-D volume. 4-D STEM diffraction was used to define atom positions within that volume (a dataset known as the specimen function) using information about the crystal space group, orientation, and lattice parameters. Individual isotopic nuclear spins are accurately placed within a semiconductor quantum do to within 0.05 Anstroms.

More work needs to be done using correlative TEM and APT to achieve ASAT, including demonstrating the ability to capture structural features such as interfaces and defects as well as 100% efficiency ion detectors. In the near future, ASAT will be achieved through integration of 100% efficiency ion detectors, improved data handling algorithms, and integration of TEM and APT into a single instrument.

5:00pm **AS+EM+SE-TuA-9 Investigating 2d-Materials Using Correlative Spectroscopy & Microscopy***, **Tim Nunney**, R. Simpson, P. Mack, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this presentation, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

5:20pm **AS+EM+SE-TuA-10 Surface Analysis in Fujifilm Electronic Materials Research & Development Laboratory: Applications on Chemical Mechanical Planarization***, **Hong Piao,*** FUJIFILM Electronic materials USA., Inc.*; Y. Liang, K. Huang, B. Duong, J. McDonough, Y. Zhang, H. Lee, B. Hu,* FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization (CMP) is a chemical reaction assisted polishing process in the semiconductor manufacturing industry. It has played a key role on integrated circuit (IC) manufacturing to anisotropically remove overburden material or specific layers in the film stacking and to planarize the topography at the wafer surface. Specific slurry formulations have been designed towards to the device structure and materials to be polished. The surface chemical processes at the interface of the wafer/slurry/pad have significant influence on the CMP performance. As device geometries are continuously shrinking as well as the introduction of new interconnect materials, the technological requirements on CMP performance have become more stringent. Thus, in-depth understanding of surface chemical processes which occur during polishing remains essential to the improvement of slurry design, the development of next-generation CMP processes and post-CMP cleaning applications.

Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of “nano-structured” materials in other fields.Surface analysis tools (XPS, Tof-SIMS and AFM) at FUJIFILM Electronic Materials U.S.A., Inc. combined with other complementary testing methods have already shown great promise as a means of achieving fundamental knowledge to the mechanisms involved in CMP processes [1].

This review continues to highlight the promising role that surface chemical analysis methods can and should play in understanding the complex interplay that drives design of CMP slurry formulation for contributions to the CMP technology. Examples describing the CMP characterization have been given in several aspects that are growing in importance: (1) Cu, Co and Ru CMP, (2) Defects (organic residues,metal contaminants and particles) removal in a post-CMP cleaning process and (3) CMP consumables: root cause analysis of pad stains.

[1]Hong Piao, Yannan Liang, James McDonough, Tawei Lin, Hyosang Lee, Carl Ballesteros, Eric Turner, Abhudaya Mishra and Richard Wen, “*Industrial Applications of Surface Science in Chemical mechanical Planarization*”, The AVS 65th International Symposium, Oct. 21-26, 2018, Long Beach, California.

5:40pm **AS+EM+SE-TuA-11 Investigating GeTe as an Ovonic Threshold Switch with Spectroscopic and Electronic Techniques***, **Melissa Meyerson,** M. Kalaswad, M. King, D. Adams, J. Custer, P. Kotula, M. Rodriguez, S. Rosenberg,* Sandia National Laboratories

Ovonic threshold switches (OTS) are a class of two or three terminal devices that exhibit a sharp transition between resistive and conductive operating regions. This transition is temporary, with the device reverting to a resistive state once bias is de-asserted from the device. The volatile resistive behavior makes OTS devices very attractive as select devices for phase change memory, voltage controlled tunable filters, and other applications. Metal telluride thin films show unique temperature dependent characteristics that may make them good materials for OTS devices. In this study, we examine the effect of annealing temperature on the chemical, physical, and electronic properties of GeTe thin films including exploring changes in crystallinity, chemical composition, and switching behavior. More specifically, X-ray photoelectron spectroscopy shows a chemical transition that occurs between 125 °C and 150 °C that results in an increase in metallic Ge and decrease in metallic Te relative to the concentration of GeTe present. Similarly, X-ray diffraction shows a transition from amorphous to crystalline GeTe around 160 °C. The films are further characterized with transmission electron microscopy, energy dispersive X-ray spectroscopy, and surface electronic measurements including ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy to determine the band gap.

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6:00pm **AS+EM+SE-TuA-12 Multi-Technique Analysis of Organic and Inorganic Semiconductors for Composition and Electronic Information***, **Paul Mack,*** Thermo Fisher Scientific, UK*; M. Modreanu,* Tyndall National Institute-University College Cork, Ireland

Photoelectron spectroscopy has been used for many years to analyse the elemental and chemical composition of a broad range of industrially relevant materials, from polymers to semiconductors.In recent years, with the development of novel organic and inorganic semiconductors, there has also been an increasing demand to measure electronic parameters alongside the elemental and chemical state information.

In this work, complementary electron spectroscopic techniques were used to comprehensively characterise organic and inorganic semiconductors for composition and electronic properties.X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental and chemical composition of the organic semiconductor, P3HT, and a range of ferroelectric films with the general formula, $Hf_xZr_yO_z$.Ultraviolet photoelectron spectroscopy (UPS) and reflection electron energy loss spectroscopy (REELS) were then used together to measure the ionisation potential, band gap and electron affinities of those samples.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis,** S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman,* ***Monika Blum**,* LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020. [2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL1+AS+EM-TuA

Emerging Technological Advances and Breakthroughs of Spectroscopic Ellipsometry

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

2:20pm **EL1+AS+EM-TuA-1 Terahertz to Vacuum Ultraviolet Ellipsometry Characterization of Spin, Lattice, Strain, Free Charge Carrier, Dielectric Constants, Exciton and Band-to-Band Transition Properties in Ultrawideband Gap Alpha and Beta Aluminum Gallium Oxide Semiconductor Alloys***, Mathias Schubert,* *R. Korlacki, M. Stokey,* University of Nebraska-Lincoln*; A. Mock,* Weber State University*; M. Hilfiker,* University of Nebraska-Lincoln*; J. Knudtson,* University of Nebraska-Lincoln, USA*; U. Kilic,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight, P. Kuehne,* Linkoping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Two phases of ultrawideband gap semiconductor gallium oxide emerge in composition with aluminum, the rhombohedral alpha and monoclinic beta phase of AlGaO. Progress in epitaxial deposition provides quality materials investigated currently with large efforts. Both phases permit access to ultrawideband gap properties reaching approximately 9 eV with sapphire. We employ a wide range of ellipsometry techniques covering 100 GHz to approximately 9.5 eV, including magnetic fields and density functional theory calculations. We provide an overview of current knowledge of properties for both compounds, discussing strain-stress relationships, evolution of phonon mode and band to band transition behaviors, dielectric constants, indices of refraction, anisotropy, and free charge carrier and defect properties [1-8]. We report on a new hyperbolic shear polariton formation in monoclinic Ga2O3 [9]. We also report on initial results of our newly developed instrumental approach for defect characterization in quantum materials, THz electron paramagnetic resonance ellipsometry for ultrahigh field and high resolution frequency spin detection and analysis in epitaxial semiconductor layer systems [10]. [1] M. Stokey et al., Phys. Rev. Materials 6, 014601 (2022). [2] M. Hilfiker et al., Appl. Phys. Lett. 118, 062103 (2021). [3] M. Hilfiker, U. Kilic, M. Stokey, R. Jinno, Y. Cho, H. Grace Xing, D. Jena, R. Korlacki, and M. Schubert, Appl. Phys. Lett. 119, 092103 (2021). [4] R. Korlacki, M. Stokey, A. Mock, S. Knight, A. Papamichail, V. Darakchieva, and M. Schubert, Phys. Rev. B 102, 180101(R) (2020). [5] P. Gopalan, S. Knight, A. Chanana, M. Stokey, P. Ranga, M. Scarpulla, S. Krishnamoorthy, V. Darakchieva, Z. Galazka, K. Irmscher, A. Fiedler, S. Blair, M. Schubert, and B. S. Rodriguez, Appl. Phys. Lett. 117, 252103 (2020). [6] M. Hilfiker, U. Kilic, A. Mock, V. Darakchieva, S. Knight, R. Korlacki, A. Mauze, Y. Zhang, J. Speck, and M. Schubert, Appl. Phys. Lett. 114, 231901 (2019). [7] J. A. Spencer, A. L. Mock, A. G. Jacobs, M. Schubert, Y. Zhang, and M. J. Tadjer, Appl. Phys. Rev. 9, 011315 (2022). [8] R. Korlacki, J. Knudtson, M. Stokey, M. J. Hilfiker, V. Darakchieva, and M. Schubert, Appl. Phys. Lett. 120, 042103 (2022). [9] N. Passler, X. Ni, G. Hu, J. R. Matson, M. Wolf, M. Schubert, A. Alù, J. D. Caldwell, T. G. Folland, and A. Paarmann, Nature 602, 595 (2022). [10] M. Schubert, S. Knight, S. Richter, P. Kuehne, V. Stanishev, A. Ruder, M. Stokey, R. Korlacki, K. Irmscher, P. Neugebauer, and V. Darakchieva, Appl. Phys. Lett. 120, 102101 (2022).

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-TuA

Bridging Gaps I: Structural and Dynamic Effects in Catalysis

Moderator: Dan Killelea, Loyola University Chicago

2:20pm **HC+AS+SS-TuA-1 Fundamental Studies of C1 Catalysis on Metal-oxide and Metal-Carbide Interfaces***, **Jose Rodriguez,*** Brookhaven National Laboratory **INVITED**

The transformation of CO_2 and CH_4 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of this highly stable molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task have usually trouble binding CO_2 or CH_4 and, thus, low catalytic activity. Here, we will discuss a series of in-situ studies investigating different mechanisms or approaches for C-O and C-H bond activation. They illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 or CH_4 into methanol. CeOx/Cu(111), Cu/CeOx/TiO_2(110) and Cu/TiC(001) exhibit an activity for the $CO_2 \rightarrow CH_3OH$ conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Cu-TiC interfaces, the combination of metal and oxide (or carbide) centers affords complementary chemical properties that lead to special reaction pathways for methanol synthesis. Metal-oxide and metal-carbide interfaces also can be tune for the activation and conversion of CH_4.

3:00pm **HC+AS+SS-TuA-3 Atomic Scale Studies of Chromium Species on Iron Oxide Surfaces***, **Moritz Eder,*** TU Wien, Austria*; P. Sombut,* University of Vienna, Austria*; C. Wang, L. Puntscher, A. Rafsanjani-Abbasi, M. Meier, J. Pavelec, G. Franceschi, M. Riva,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; M. Schmid, U. Diebold, G. Parkinson,* TU Wien, Austria

Chromium (Cr) ferrite catalysts are industrially employed for the water gas shift reaction in order to provide large amounts of molecular hydrogen.[1] However, the European REACH legislation demands that hexavalent Cr be banned from all catalysts used in industrial processes due to its toxicity. Consequently, alternative metals are sought to fulfill the role of Cr species in the corresponding compounds.[2] It is therefore necessary to obtain a fundamental understanding and characterization of Cr on iron oxides.

In this talk, we present the investigation of Cr species on Fe_3O_4(001) by means of STM and XPS at room temperature. We show the behavior during exposure to water gas shift reactants (i.e., CO and H_2O) and upon high temperature treatment. The latter is of utmost importance since the water gas shift reaction is conducted at temperatures up to 500°C.[1] The results are compared to the behavior of other transition metals and discussed with respect to implications for applied catalysis.[3]

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[2] Glassner, *Int. Surf. Technol.***14**, p. 36, (2021)

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3:20pm **HC+AS+SS-TuA-4 Investigation of CO Oxidation on Oxygenated Rh(111) Surfaces with RAIRS***, **Elizabeth Jamka,*** *D. Killelea,* Loyola University Chicago

Surface IR spectroscopy is a quantitative technique that also provides information about the binding sites and chemical environments of the adsorbed CO molecules. In this research we are able to interface a FTIR to the ultra-high vacuum (UHV) chamber as a non-destructive and highly sensitive surface analysis technique. Because IR measurements can be performed in UHV conditions, interference from atmospheric species are avoided, while enabling investigation of catalytic systems, like carbon monoxide (CO) to carbon dioxide (CO_2) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO_2 on oxidized Rhodium (Rh) will be utilized as a probe reaction. Studying CO oxidation on different Rh surfaces will provide atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes. This research focuses on CO sticked to clean Rh(111), (2x1)-O/Rh(111), and (2x1)-O + RhO_2/Rh(111). Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.

4:20pm **HC+AS+SS-TuA-7 Molecular Beam Surface Reaction Experiments with Chiral Molecules***, Tim Schäfer,* Georg August University, Goettingen, Germany **INVITED**

Chirality is a feature of asymmetry describing the geometrical property of objects that cannot be mapped onto their mirror images like our hands as classic example. In chemistry, one observes chirality on the molecular level: two mirror images of chiral molecules (enantiomers) have only little difference in the structure, but this might cause a vast change in the biological activity.

Unfortunately, a fundamental understanding of chemical processes in chiral environments is challenging, as enantiosensitive detection methods must introduce chirality to distinguish enantiomers. Until recently, enantiospecific assignment of chiral gas phase molecules at low concentrations was not even possible. In the last decade, new enantiosensitive detection techniques have been invented based on photoionization of molecules (Photoelectron Circular Dichroism, PECD). Our group contributed to these advances by developing a unique technique that combines PECD with surface science. This approach allows the investigation of dynamics and kinetics of surface reactions of chiral molecules at the gas surface interface.

We use this technique for studies on heterogeneously catalyzed chiral surface reactions like the partial oxidation of olefins to epoxides on metal surfaces. For this, we combine PECD measurements with velocity resolved kinetics experiments, providing enantiosensitive information about reaction mechanisms at surfaces.

5:00pm **HC+AS+SS-TuA-9 A Local View on the Influence of Solvent and Product on the Reactivity of Surface-Catalyzed Reactions***, **Karina Morgenstern,*** Ruhr Universität Bochum, Germany **INVITED**

Though largely influencing the efficiency of a reaction, the molecular-scale details of the local environment of the reactants are experimentally inaccessible hindering an in-depth understanding of a catalyst's reactivity, a prerequisite to maximizing its efficiency. We introduce a method to follow individual molecules and their largely changing environment during laser-induced reactions. The method is illustrated with a single-molecule resolution on two examples, the dissociation of halogenated benzene molecules adsorbed on ice [1] and of CO_2 on two catalytically relevant surfaces, Ag(100) and Cu(111)[2]. Dissociation of halobenzene is triggered by delocalized excess electrons. The adsorption on ice sufficiently lowers the energy barrier for the transfer between themolecular orbitals to facilitate dissociation of bromo- and chloro- but not of fluorobenzene at cryogenic temperatures.For the CO_2dissociation, we reveal how the reactant's surroundings evolve with progressing laser illumination and with it their propensity for dissociation. Our results shed light on the influence of solvent and products on reaction yields on the nanoscale.

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[2] M. Vyshnepolsky, Z.-B. Ding, P. Srivastava, P. Tesarik, H. Mazhar, M. Maestri, K. Morgenstern, Angew. Chem. Int. Ed. 60, 18217-18222 (2021)

5:40pm **HC+AS+SS-TuA-11 Enhanced Catalytic Selectivity Due to Topographically Reduced Work Function of Carbon Nanospikes***, **Arthur P. Baddorf,*** Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A. Rondinone,* Center for Integrated Nanotechnologies, Los Alamos National Laboratory*; D. Hensley,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Carbon nanospikes show excellent Faradaic efficiency and selectivity for electrochemical conversion of technologically important reactions, including CO_2 to ethanol in the presence of Cu [1] and N_2 to ammonia in the presence of Li [2]. Rates are higher than for other aqueous electrochemical approaches, including other low-dimensional carbon nanomaterials such as nanotubes, fibers, and foams, and much greater than for flat carbon surfaces. The essential attribute appears to be the sharp spike topography at which electric fields are enhanced. Transmission electron microscopy images reveal that films consist of a high density of nanospikes each 50-80 nm in height and terminated with a sharp tip of radius ~1 nm, i.e. a very high curvature.

We have explored the electric fields at the nanospikes by measurements of the absolute work function in comparison that of other carbon geometries using ultraviolet photoemission spectroscopy (UPS). As samples were characterized after transfer through air, surface cleanliness was monitored with x-ray photoelectron spectroscopy (XPS). Annealing as-grown samples above 275 °C was required to produce a clean surface which has a 4.13 eV work function, a half volt lower than that of flat graphite. This reduction supports the idea that a strong electric field is generated by the nanospike topography which contributes to the electrochemical activity.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values following exposure increased to 4.19 eV for hydrocarbons, 4.30 for air, 4.42 for water, and 4.48 for oxygen. Blunting the spikes, by exposure to an oxygen plasma, argon sputtering, or annealing to 800 °C results in a work function close to that of flat graphite, 4.62 eV. An unusual double onset in the UPS secondary electron intensity is observed after absorbing hydrocarbons on clean nanospikes. This double onset has not been reported on metal surfaces and appears to be unique to carbon substrates. The energy difference between the two onsets, about 0.4 eV is close to that of a typical C-H stretch in hydrocarbons suggesting the lower energy onset may originate in inelastic scattering of photoelectrons.

* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

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6:00pm **HC+AS+SS-TuA-12 HC Graduate Student Finalist Talk: Enhanced Descriptor Identification and Mechanic Understanding for Catalytic Activity using Data-Driven Framework: A Case Study of CO Hydrogenation over Cu-Based Single Atom Alloys***, **Wenjie Liao,*** Stony Brook University/Brookhaven National Laboratory*; P. Liu,* Brookhaven National Laboratory and State University of New York at Stony Brook

Accurate identification of descriptors for catalytic activities has long been essential to the in-depth mechanic study of catalysis and recently to set the basis for catalyst screening. However, commonly used derivative-based local sensitivity analysis methods suffer from low accuracy in predictability. This study reports an enhanced approach to accurately identifying the descriptors from a kinetic dataset using the machine learning (ML) surrogate model. The CO hydrogenation to methanol over Cu-based single atom alloys was taken as a case study.

Our model captures not only the contribution from individual elementary steps (i.e., first-order descriptors), but also the interaction between relevant steps within a reaction network (i.e., second-order descriptors), which was found to be essential for accuracy. As a result, six effective descriptors are identified, which are accurate enough to ensure the trained gradient boosted regression (GBR) model for well prediction of the methanol turn-over-frequency (TOF) over metal (M)-doped Cu(111) model surfaces (M = Au, Cu, Pd, Pt, Ni). More importantly, going beyond the purely mathematic ML model, the catalytic role of each identified descriptor can be revealed by using the model-agnostic interpretation tools, which enhances the mechanic insight into the promoting effect of alloying. The trained GBR model outperforms the conventional derivative-based methods in terms of both predictability and mechanic understanding.

The proposed data-driven framework allows one to identify key descriptors beyond rate-limiting steps while clearly depicting how each identified key descriptor would affect the catalytic activity when more than one activation energies were tuned. This approach can be applied to other reactions and catalysts, which opens alternative possibilities toward accurate descriptor-based rational catalyst optimization

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS1+2D+AS+EM+QS+SS-TuA

Operando Catalysis and Energy Systems

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **LS1+2D+AS+EM+QS+SS-TuA-1 In-situ/Real-time XPS Study of Electrochemical Reactions in All-solid-state Thin-film Lithium-Ion Batteries*, Takuya Masuda,*** National Institute for Materials Science, Japan **INVITED**

All-solid-state lithium-ion batteries (ASSLIBs) are one of the most promising next generation rechargeable batteries because of their very high safety and reliability. Understanding of the mechanism of electrochemical reactions and related physicochemical phenomena is very important for improving cell performances and durability. Application of ex-situ techniques to multiple samples disassembled from cells after certain charge/discharge cycles often results in misinterpretation due to the variation of samples and undesired side effects during sample transfer between battery test environment and characterization apparatus. Thus, various in-situ techniques which can be applied to the same position of the same sample kept at a certain charge/discharge state have been developed for hierarchical understanding of a series of electrochemical events interplaying with each other. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the composition of reaction products, chemical state, and electronic structure of sample surfaces. By tuning the energy of incident x-rays, it also enables us to conduct the depth-resolved analysis of surfaces and interfaces including those buried with solid thin films. Recently, we developed an in-situ XPS apparatus equipped with a bias application system and a vacuum suitcase for sample transfer,[1] and applied it to the electrochemical lithiation/delithiation reactions of an amorphous Si thin film electrode sputter-deposited on a solid electrolyte sheet.[2] The chemical state of Si electrode changing during lithiation/delithiation processes was successfully tracked by sequential XPS measurements in the regions of Li 1s, C 1s, O 1s, and Si 2p. Not only lithium silicide (Li_xSi) which reversibly responds to the lithiation/delithiation but also irreversible species such as lithium oxides, lithium silicates and lithium carbonates were formed due to the lithiation of the Si electrode. Moreover, a rapid spectral change attributable to the phase transition of a crystalline Li_xSi to an amorphous phase was observed in the successive delithiation after preceding lithiation up to certain level. Based on the state of charge, Li content x in Li_xSi, and positions of XPS peaks, we summarized the lithiation/delithiation mechanism in Si electrodes. Further details will be presented.

[1] R. Endo, T. Ohnishi, K. Takada, T. Masuda, Journal of Physics Communications, 2021, 5, 015001.

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3:00pm **LS1+2D+AS+EM+QS+SS-TuA-3 Interaction of Molecular Nitrogen with Vanadium Oxide in the Absence and Presence of Water Vapor at Room Temperature: Near-Ambient Pressure XPS***, S. Nemsak,* Lawrence Berkeley National Laboratory*; **Kabirat Balogun**, P. Chukwunenye, T. Cundari, P. Bagus, J. Kelber,* Department of Chemistry, University of North Texas

Interactions of N_2 and H_2O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N_2/H_2O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N_2 partial pressures between 10^{-9} Torr and 10^{-1} Torr using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N_2-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N_2 and equal pressures of N_2 and H_2O vapor, up to a N_2 partial pressure of 10^{-1} Torr. In the absence of H_2O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10^{-9} Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of equilibrium with gas phase N_2. In the presence of equal pressures of N_2 and H_2O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10^{-1} Torr N_2 partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N_2-surface binding in the absence of N_2 overpressure are consistent with N_2 binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N_2/H_2O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to "shake" and normal transitions at 401 eV and 398.7 eV, respectively, for N_2 bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N_2 pi* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N_2 -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

Acknowledgement:
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No. DE-AC02-05CH11231. Work at UNT was supported in part by the NSF through grants DMR-2112864 (JAK, TRC), and via NSF support for the UNT CASCaM HPC cluster via Grant CHE-1531468. PSB was supported by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE through its Geosciences program at PNNL.

3:20pm **LS1+2D+AS+EM+QS+SS-TuA-4 Catalysts Caught in the Act: an Operando Investigation of Copper during CO_2 Hydrogenation*, Elizabeth Jones,*** University of Oxford, UK

Amongst the foremost challenges in mitigating global warming are replacing fossil fuels with renewable alternatives, and storing/using carbon captured from CO2-emitting processes. Methanol production by CO2 hydrogenation promises a possible solution to both of these issues, particularly if H2 can be obtained through water electrolysis. When the resulting methanol is used as a fuel an equivalent amount of CO2 is released making it a “net-zero” fuel alternative. CO2 hydrogenation is performed industrially using a CO2/H2 mix at 200-300oC, 50-100 bar with a Cu-based catalyst, and the addition of CO is known to increase the methanol yield. However, mechanistic understand of this reaction and the role played by CO remains limited. Soft X-ray spectroscopies can provide details on the chemical state of copper to uncover the chemistry behind this reaction, however the typical requirement for measurement under high vacuum constrains how realistic these studies can be. There has been much recent development on improving operando techniques to enable heterogeneous catalytic reactions to be studied under realistic pressure conditions (E. S. Jones et al., in Ambient Pressure Spectroscopy in Complex Chemical Environments, 2021, ACS Symposium Series, vol. 1396, ch. 8, 175-218). A promising approach is to use an environmental cell which encloses the desired gas and separates it from the high vacuum environment, using an X-ray transparent window (R. S. Weatherup, J. Phys. Chem. Lett., 2016, 7, 1622-1627).

Using a custom-designed high pressure environmental cell we have studied model Cu catalysts using operando NEXAFS in total electron yield mode up to pressures of 1 bar and temperatures of 200oC. A thin Cu film was deposited onto a Si3N-4 membrane which acted to seal the high pressure gas within the cell and as a transparent window for incident X-rays. The aim of the study was to investigate how the Cu oxidation states varied when exposed to H2 and CO2 in different sequential order and how the introduction of CO can further influence the chemical state of Cu. It was found that H2 can provide a protective barrier to oxidation from CO2 when dosed first, however if H2 was added after CO2 it is unable to return the surface to its metallic state where CO is then required for reduction. This offers an insight into why CO plays an important role in the industrial production of methanol. Additionally, advances in sealing of the environmental cell enabled high pressures to be achieved at elevated temperatures, allowing this approach to be extended to more industrially-relevant conditions.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS2+2D+AS+TF-TuA

Role of Defects in Materials

Moderator: Takuya Masuda, National Institute for Materials Science, Japan

4:20pm **LS2+2D+AS+TF-TuA-7 Visualizing Complex Many-Body Phenomena in 2D Materials Based Heterostructures and Devices***, **Jyoti Katoch**,* Carnegie Mellon University **INVITED**

Two-dimensional (2D) materials offer the freedom to create novel condensed matter systems, with unique properties, by mechanically assembling different (or same) 2D materials layer-by-layer to form atomically sharp vertical or lateral heterostructures. The van der Waals (vdW) heterostructures with small lattice mismatch and a relatively small twist angle between the constituent layers, have shown to exhibit coexisting complex phases of matter including Mott insulating state, superconductivity, bound quasiparticles, and topological states. The advent of the state-of-the-art angle-resolved photoemission spectroscopy with high spatial resolution (micro- and nano-ARPES) and the ability to perform these measurements on fully functional devices, has made it possible to directly probe many exotic physical phenomena in 2D based material systems. In this talk, I will discuss the utilization of the nanoARPES to investigate the highly tunable many-body effects in 2D based heterostructures and their devices.

5:00pm **LS2+2D+AS+TF-TuA-9 Dynamic Grating Development for Neutron Imaging Across Multiple Length Scales***, **Sarah M. Robinson**, R. Murphy, J. LaManna, C. Wolf,* National Institute of Standards and Technology (NIST)*; Y. Kim, M. Daugherty,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; M. Huber, P. Bajcsy, P. Kienzle, K. Weigandt, D. Hussey, N. Klimov,* National Institute of Standards and Technology (NIST)

Current neutron scattering techniques can provide sample structural information on the length scales of nano- to micrometers, but it is challenging to investigate the hierarchical structures found in non-homogeneous samples. We are developing a far-field grating interferometer (INFER) to nondestructively study the microstructures of samples averaged over a voxel size of 50 µm. In order to perform far-field neutron interferometry across multiple length scales, a large number of source grating periods are used to multiplex the signal and impart the required transverse quasi-coherence. To eliminate the need of fabricating, installing, and aligning a new static source grating for each period, we have developed a DynAmic ReconfIgUrable Source grating (DARIUS). DARIUS is a wafer-scale silicon microfluidic device that allows for the real-time adjustment of the grating period, ranging from 20 µm to 20,000 µm, with the potential to replace more than 500 static source gratings. In DARIUS, each of 5,000+ individual grating channels can be selectively infilled with a neutron and x-ray absorbing fluid to modulate the neutrons, creating an absorbing grating with an effective period based on the locations of the opaque fluid. A key part of DARIUS is a diffraction grating layer fabricated on a 100 mm Si wafer. In this layer, the grating channels are etched in silicon with period of 20 µm and depth of 125 µm, corresponding to a channel volume of enough fluid to locally attenuate the neutron beam. We have previously demonstrated that we can selectively fill 128 active channels with x-ray absorbing solution and, with that, modulate in real time an x-ray beam. Our next prototype, DARIUS-2.0, has an active area of 40.96 mm x 51.20 mm with 2,560 active channels on a single side of a 100 mm Si wafer. The channels are sealed by wafer-scale eutectic bonding to a capping wafer with vias for well and pumping port access. We will present results on initial testing of DARIUS-2.0 with x-ray imaging and progress on scaling up to a double-sided grating device to be incorporated in INFER to unlock the ability of analysis over a wider range of length scales.

5:20pm **LS2+2D+AS+TF-TuA-10 Dynamics, Stability and History-Dependence of Magnetic Skyrmions in the 2D van der Waals Magnets Fe_xGeTe_2***, **Kai Litzius**, M. Birch, L. Powalla, S. Wintz,* Max Plank Institute for Intelligent Systems, Germany*; M. Weigand,* 4Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*; K. Kern, M. Burghard, G. Schutz,* Max Plank Institute for Intelligent Systems, Germany **INVITED**

Recently, the combination of 2-dimensional (2D) magnetism [1] with the field of spintronics, i.e. the manipulation of magnetic states with electric currents, has started to gain much traction in modern solid-state physics. The prospect of highly efficient low-dimensional devices, extreme ease to fabricate versatile heterostructures by stacking of separate individual layers, and the report of chiral topological magnetic solitons in 2D itinerant ferromagnets have further enhanced the field's interest in this fascinating class of materials. Requirements for technological implementation, however, are generally to realize both the fabrication of nanoscale devices and to understand different potential ways to tailor the material parameters and ferromagnetic ordering temperatures [2,3] in desirable ways.

In this work, we utilize real-space imaging of the magnetic texture in thin flakes of the van der Waals magnets Fe_xGeTe_2 to determine magnetic phase diagrams of various exfoliated films with varying compositions. We furthermore realize devices for local injection of skyrmions by means of vertical nanocontacts. Our findings show besides complex, history-dependent magnetization states also that changes in the composition and crystalline structure significantly alter the magnetic behavior and may be used to tune the stability of skyrmions or other magnetic textures in these novel magnetic systems. Ultimately, the choice of composition and nucleation mechanism result in a selective stabilization of a variety of (meta-) stable magnetic configurations. Especially individual skyrmions can then be injected by targeted current pulses through a nanocontact. Our findings open novel perspectives for designing van der Waal heterostructure-based devices incorporating topological spin textures.

References:

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2. May A. F. et al. (2019). Ferromagnetism Near Room Temperature in the Cleavable van der Waals Crystal Fe5GeTe2. ACS Nano 13, 4436–4442.

3. Chen H. et al. (2022) Revealing room temperature ferromagnetism in exfoliated Fe5GeTe2 flakes with quantum magnetic imaging. 2D Materials 9 025017.

Plasma Science and Technology Division
Room 315 - Session PS2+AS+SS-TuA

Plasma-Surface Interactions

Moderators: Pingshan Luan, TEL Technology Center America, **Kenji Maeda**, Hitachi High Technologies America Inc.

2:20pm **PS2+AS+SS-TuA-1 Selective Mask Deposition Using $SiCl_4$ Plasma for a Highly Selective Etching Process***, **Miyako Matsui**,* Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Tech Corp., Japan **INVITED**

The local cell size of logic devices has been continuously shrinking at a scaling rate of about 0.48 per 2 years. Extreme ultraviolet (EUV) lithography is a key technology for pitch scaling, though the pitch scaling rate has been slowing down since 2010. To boost the scaling, design technology co-optimization (DTCO) has been developed by using various kinds of self-aligned processes. However, process challenges exist for both technologies. Etching processes using thin EUV resists require extremely high selectivity and precise control of critical dimensions. Selective etchings for DTCO require high selectivity between layers having a similar material composition. In both cases, selective deposition for forming protective layers only on unetched materials can solve these process challenges and achieve extremely highly selective etchings.

In this study, we investigated a selective deposition process for forming protective layers on top of masks generated by a microwave-ECR etching system. A deposition layer was formed only on SiO_2 masks without forming an unnecessary deposition layer on Si surfaces of etching area, such as bottoms of the patterns and isolated etching area. This process effectively achieves extremely highly selective etchings by selectively forming the protective layers prior to the etching procedure in the same chamber.

We suggested a process for selectively forming protective layers on a SiO_2 without forming on a Si etching area by using a $SiCl_4/H_2/Cl_2$ plasma. Top surfaces of the materials needed to be cleaned before forming the protective layer. Selectivity is thought to be provided by the difference in $SiCl_x$ desorption processes. On the Si surface, adsorbed $SiCl_x$ easily desorbed again by reacting with Cl generated from the plasma. On the other hand, adsorbed $SiCl_x$ on SiO_2 was thought to be more difficult to desorb by reacting with Cl due to Si-O having larger binding energy than Si-Si. After the deposition layer was selectively formed on the SiO_2 mask, the layer was oxidized using an O_2 plasma treatment to improve the etching resistance during the Si-etching. The O_2 plasma treatment time was controlled not to prevent the Si substrate from being etched during the Si-etching. We found the optimum O/Si concentration of oxidized protective layer was about 0.4 from X-ray photoelectron spectra (XPS) analysis.

We also demonstrated the selective deposition to etch a line-and-space pattern with a SiO_2 mask. In this process, selective deposition, oxidation, and Si etching were cyclically carried out. The extremely highly selective etching was achieved using the selective deposition without forming an unnecessary deposition on an isolated Si area.

3:00pm **PS2+AS+SS-TuA-3 On the Self-bias Voltages at Sintered Yttrium Oxyfluoride (Y-O-F) and Y_2O_3 During Plasma Irradiation and Their Etching Rates due to Ion Bombardment***, **Tetsuya Goto**, Y. Shiba,* Tohoku University, Japan*; A. Teramoto,* Hiroshima University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (Y-O-F) has been received much attention as the bulk and/or coating materials for functional components used in the plasma process chamber in semiconductor manufacturing, because chemical component stability of Y-O-F against various corrosive plasmas is better than that of widely used Y_2O_3 [1-3]. In addition to the chemical component stability, etching rate of these materials is also an important issue when particle problem and lifetime of the components are considered in industry. Previous report has shown that the etching rate of Y-O-F and Y_2O_3 due to plasma irradiation is almost the same level [2]. On the other hand, we reported that, the etching rates of the sintered Y-O-F due to the Ar ion beam irradiation (without plasma) was clearly smaller than that of Y_2O_3 [3]. We speculated that such tendency was caused by higher atomic number density of Y-O-F than that of Y_2O_3. Thus, the etching behavior of Y-O-F and Y_2O_3 was different between the cases of the ion beam irradiation and the plasma irradiation.

In this report, to understand the observed difference in more detail, we measured self-bias voltage V_{dc} of surfaces of Y-O-F and Y_2O_3 samples set on Si wafer in 13.56-MHz excited capacitive coupling Ar plasma. Here, V_{dc}, which is approximately an acceleration voltage of ions, is a good parameter to estimate ion bombardment energy at the sample surface. It was found that $|V_{dc}|$ of Y_2O_3 was smaller than that of Y-O-F, suggesting that surface voltage condition was different under the normal setup of the samples for the plasma irradiation test. In this setup, etching rates of Y-O-F and Y_2O_3 due to Ar plasma irradiation were found to be almost the same.

Next, to equalize the surface voltages of Y_2O_3 and Y-O-F during the plasma irradiation as far as possible, we connected the sample surface and the Si wafer surface using electrically-conductive carbon tape. In this case, it was found that the etching rate of Y-O-F was smaller than that of Y_2O_3, showing the same behavior to the Ar ion beam etching experiment.

The results suggested that the intrinsic etching resistance of Y-O-F due to the ion bombardment is better than that of Y_2O_3. Also, the results showed the importance of how the sample was set in the plasma irradiation test to accurately estimate plasma resistance. Furthermore, it is considered that, in the actual plasma equipment, plasma resistance depends strongly on how the protect material was set or coated.

1. Y. Shiba et al, J. Vac. Sci. Technol. A, 35 (2017) 021405.

2. H. Ashizawa and K. Yoshida, Int J Appl Ceram Technol. (2021) 1.

3. T. Goto et al., J. Vac. Sci. Technol. A, 38 (2020) 043003.

4:20pm **PS2+AS+SS-TuA-7 In-Plasma Photo-Assisted Etching of Si with Chlorine Aided by an External Vacuum Ultraviolet Source***, L. Du, D. Economou, **Vincent M Donnelly**,* University of Houston

Photo-assisted etching (PAE) of *p*-type Si(100) was found to occur in a chlorine-containing, Faraday-shielded, inductively coupled plasma (ICP) with no substrate bias, attributed mainly to the vacuum ultraviolet (VUV) light generated by the plasma. Other causes for the very high etching rates can be ruled out, including ion bombardment-assisted etching and chemical etching by Cl atoms. Masked samples produced slow etching (111) facets and smooth surfaces. To provide additional evidence for the VUV-PAE mechanism, the substrate in a main Cl_2/Ar ICP was subjected to extra VUV light (mainly 104 and 106 nm Ar emission) that was generated in an independently controlled, auxiliary Ar/He ICP in tandem with the main ICP. The ICPs were separated by a tungsten mesh and a bundle of high-aspect-ratio quartz tubes in a honeycomb configuration. There was no measurable perturbation of the main plasma by the auxiliary plasma. The etching rate was found to be enhanced by 11 to 51% with the additional VUV light provided by the auxiliary ICP. Absolute measurements of the auxiliary ICP photon flux at the surface were obtained in-situ by recording photoemission yields from a Au-coated sample in place of the Si substrate. Incredibly large etching yields of 90 to 240 Si atoms-per-photon were obtained. It is argued that etching is not a result of electron-hole pair formation, but is instead ascribed to a photo-catalytic chain reaction. No etching occurs with just $Cl_{2(g)}$ and the auxiliary VUV source, hence Cl atoms produced by the main ICP are required to produce the more highly chlorinated surface required for propagation of the chain reaction.

4:40pm **PS2+AS+SS-TuA-8 Etching of Silicon Dioxide (SiO_2) Based on Remote Plasma-Based Functionalization and Electron Beam-Activation***, **Yudong Li**, K. Lin,* University of Maryland, College Park*; C. Preischl, C. Hermanns, D. Rhinow, H. Solowan, M. Budach, H. Marbach, K. Edinger,* Carl Zeiss SMT, Germany*; G. Oehrlein,* University of Maryland, College Park

Electron-beam stimulated activation of SiO_2 surfaces functionalized by remote plasma is demonstrated as a promising novel approach to achieve atomic scale etching. Compared to conventional plasma-based dry etching utilizing ion bombardment, electron-beam induced etching (EBIE) avoids ion-induced damage effects such as atomic displacement and atomic mixing. One issue with EBIE is the limited number of chemical precursors that is available to functionalize substrate surfaces without spontaneous etching.

In this work, we demonstrate a new approach that combines surface functionalization by a remote plasma source and energy deposition using an electron beam source to enable EBIE. A prototypical case is SiO_2 etching using Ar/CF_4/O_2remote plasma generated precursors and electron-beam initiated removal of the chemically reacted surface layer by low-energy electron bombardment. We evaluated the parametric dependence of SiO_2etching on remote plasma source and electron flood gun operating parameters, including radiofrequency (RF) source power, CF_4/O_2 flow composition, electron energy and emission current, respectively. Two prototypical processing cases were examined: one simultaneous and two sequential remote plasma treatment and electron beam irradiation. Material selective atomic scale etching of Si_3N_4 over SiO_2 and poly-Si over SiO_2 were demonstrated. Surface chemcial modification and etching were followed by in-situ ellipsometry measurements. Surface chemical changes were also characterized by x-ray photoelectron spectroscopy and revealed mechanistic insights for these processes.

We gratefully acknowledge the financial support of this work by ZEISS SMT GmbH.

5:00pm **PS2+AS+SS-TuA-9 Investigation of Plasma-Surface Interactions During Plasma Enhanced Atomic Layer Deposition (PE-ALD) of Silicon Nitride Using *in Situ* Surface Chemistry Measurements***, **Samuel Johnson**,* University of Texas at Austin*; J. Zhao, T. Iwao, J. Carroll, C. Schlechte, P. Ventzek,* Tokyo Electron America*; J. Ekerdt,* University of Texas at Austin

A low temperature process for silicon dielectric thin film deposition is necessary for a wide range of semiconductor process applications, including as spacers in FinFET and self-aligned multiple patterning. Using plasma enhanced atomic layer deposition (PE-ALD) with radio frequency (RF) power to deposit silicon nitride films is very promising as it lowers the deposition temperature compared to thermal atomic layer deposition; however, direct plasma enhanced processes face a difficulty of guaranteeing the conformality of film thickness and film properties on high aspect ratio, 3-dimensional device structures. Ionized plasma species have a high degree of directionality, resulting in differences between top facing and sidewall surface coverage and properties. Ion beam incoherency, which can be tuned by varying the frequency and pressure, may be used to achieve more property conformity.

To explore the PE-ALD of silicon nitride, we built a radio frequency capacitively-coupled plasma (CCP) PE-ALD chamber.Our PE-ALD process involves one half cycle of dichlorosilane (DCS) gas for silicon layer adsorption, and another half cycle of an ammonia/argon plasma for nitridation. We used three different RF frequencies in deposition experiments on planar surfaces and a 3-dimensional trench-patterned surface in a silicon substrate. We have investigated the bulk film and surface chemistry using *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* Fourier-transform infrared spectroscopy (FTIR). With increasing frequency, the overall N-H_x bonding decreased (a higher percentage of nitrogen bonds were unsaturated), and the remaining N-H_x bonds became rich in N-H_2 bonds compared to N-H bonds. Further details will be discussed on the correlations between the plasma characteristics (ion energy and angle, neutral flux, etc.), the *in situ* surface chemistry measurements, and the film properties.

5:20pm **PS2+AS+SS-TuA-10 Differences in Sidewall Chemistry for SiO_2 and Si_3N_4 after Ar/HFC or Ar/FC Plasma Processing Using High Aspect Ratio Structures**, ***Sang-Jin Chung***, University of Maryland, College Park; *P. Luan, A. Metz, M. Park,* TEL Technology Center, America, LLC, USA; *G. Oehrlein,* University of Maryland, College Park

State-of-the-art 3-dimensional memory devices utilize high-aspect-ratio (HAR) heterogeneous structures where 2 or more materials are etched simultaneously during the fabrication process. Controlling the sidewall chemistry of stacked materials etched using the same fluorocarbon (FC) or hydrofluorocarbon (HFC) process is one of the key factors for yielding excellent etch profiles. Here, we use a horizontal trench gap structure [1,2] to simulate the interaction of neutral radicals produced by FC and HFC plasma with SiO_2 and Si_3N_4 sidewalls in HAR structures for aspect ratios (AR) of up to 90. Oxide and nitride trench structures were simultaneously treated with Ar/FC or Ar/HFC plasma without RF bias and changes in film thickness were probed by ellipsometry as a function of AR. We find a variety of responses of the trench sidewalls for the remote plasma conditions, including both polymer deposition and spontaneous etching. These responses are dependent on the type of FC and HFC gases, the surfaces being exposed, and the position relative to the trench entrance. For HFC chemistry, oxide shows relatively little etching near the trench entrance followed by the presence of a very thin FC layer (<1 nm) for increasing AR. For the same conditions Si_3N_4 shows significantly more etching both near the entrance and for high AR deep in the structure. For FC plasma the behavior is different and polymer deposition is primarily seen for the high-AR trench structures. These observed behaviors are further correlated to the scalloping phenomenon commonly seen in layered ONO HAR structures. We will also discuss the surface responses with in-situ characterizations, including optical emission spectroscopy (OES), and FC deposition rate measurements seen for directly exposed SiO_2 or Si_3N_4 surfaces.

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5:40pm **PS2+AS+SS-TuA-11 Significance of Plasma-Surface Interactions in the Etch Behavior of Low-k Materials**, ***Adam Pranda***, *S. Grzeskowiak, Y. Yoshida, E. Liu, Y. Han, P. Biolsi,* TEL Technology Center, America, LLC; *K. Kobayashi, N. Ikezawa,* Tokyo Electron Miyagi Ltd., Japan

Low-k materials are an integral component in the advancement of semiconductor device performance by reducing parasitic capacitance and enabling faster device switching for a given thickness compared to traditional dielectric materials such as SiO_2. With the advances in logic scaling, low-k materials are increasingly more prominent in the structures of advanced devices. For example, low-k materials are being targeted as the inner spacer ingate-all-around (GAA) nanosheet field effect transistors. Consequently, the integration of low-k materials requires that the etch behavior of these materials be well understood so that the device structures can be reliably and reproducibly fabricated. In this study, we used a high-density plasma reactor with benchmark CF_4- and NF_3-based process chemistries to etch low-k materials including SiCN, SiOCN, and SiBCN along with reference materials including Si, SiO_2, and SiN. We utilized a characterization suite consisting of optical emission spectroscopy (OES), mass spectroscopy (MS), spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to understand the relationships between the plasma conditions (OES, MS), the evolution of the surface chemistry of the materials (XPS, ATR-FTIR), and the resulting etch behavior (SE). The etch behavior of low-k materials under a given etch process is vital for establishing the etch selectivities in multilayer structures that are required to yield complex device geometries. For example, we found a correlation in the relative magnitude of OES trend for the CN emission at 387nm to the low-k material etch rate, which suggests that preferential sputtering of the nitrogen and possibly carbon from the sample is one of the main pathways for the etching of nitrogen-containing low-k materials. Identifying the underlying mechanisms for the etch behaviors of low-k materials will provide key guidance into the development of etch processes that integrate these materials in current and future device structures.

6:00pm **PS2+AS+SS-TuA-12 Low Temperature Superpermeability in Metal Foils Exposed to Hydrogen Plasma**, ***Chao Li***, *A. Job,* Colorado School of Mines; *M. Shimada, T. Fuerst,* Idaho National Laboratory; *D. Way, C. Wolden,* Colorado School of Mines

The hydrogen isotopes tritium (T) and deuterium (D) are leading fuels for use in future fusion reactors. In these reactors they combine to form He and an energetic neutron in a high density, magnetically confined plasma. Metal foil pumps are a technology to extract the unreacted isotopes from the He ash in the plasma exhaust and return them to the plasma in a process known as direct internal recycling. Hydrogen separation membranes typically work through a dissociative adsorption - atomic diffusion - recombinative desorption mechanism that relies on a hydrogen partial pressure gradient. Unlike molecular hydrogen, energetic H atoms and ions can bypass the dissociation/absorption step and directly enter the metal. This leads to hydrogen fluxes that can be orders of magnitude greater than expected from Sievert's law, a condition described as superpermeability. In this study, we investigate the superpermeability of various metal foils (PdAg, V and α-Fe) exposed to inductively coupled H_2 plasma operating at low temperature (50-200 ^oC) and the results are compared to a fundamental model accounting for individual steps in hydrogen permeation. Systematic variation of foil temperature and plasma parameters were used to illuminate the key rate limiting steps in the mechanism. Interfacial treatments including oxidation, plasma cleaning, and the deposition of nanoscale interfacial layers were used to modify surfaces to improve the hydrogen permeation of metal foils. Auger and AFM characterization were used to study the surface elemental composition and metal surface roughness, respectively. Both H_2 and D_2 plasmas were employed to better understand isotope effects. V foils with symmetric Pd deposition on both sides showed comparable permeation performance to PdAg foil with hydrogen flux exceeding 10^{20} m^{-2} s^{-1}. On the other hand, plain α-Fe foils showed very stable, but lower (10^{19} m^{-2} s^{-1}) hydrogen flux performance in repeated tests. Our findings suggest that V and α-Fe with appropriate surface modification are promising candidates for use as metal foil pumps for direct internal recycling of DT fuels in future fusion reactors.

Surface Science Division
Room 319 - Session SS+2D+AS-TuA

Structure, Adsorption and Reaction at 2D Material Surfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, Argentina, **Arthur Utz**, Tufts University

2:20pm **SS+2D+AS-TuA-1 Chemically Identifying Single Adatoms with Single-Bond Sensitivity During Oxidation Reactions of Borophene**, *L. Li, N. Jiang,* ***Sayantan Mahapatra***, University of Illinois - Chicago

The chemical interrogation of individual atomic adsorbates on a surface significantly contributes to understanding the atomic-scale processes behind on-surface reactions. However, it remains highly challenging for current imaging or spectroscopic methods to achieve such a high chemical spatial resolution. Here we show that single oxygen adatoms on a boron monolayer (i.e., borophene) can be identified and mapped via ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. With this capability, we realize the atomically defined, chemically homogeneous, and thermally reversible oxidation of borophene via atomic oxygen in UHV. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties. In addition to offering atomic-level insights into the oxidation of borophene, this work demonstrates UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

2:40pm **SS+2D+AS-TuA-2 Tailoring the Interfacial Properties of 2D Transition Metal Silicates on Metal Supports**, *N. Doudin, K. Saritas,* Yale University; *J. Boscoboinik, G. Li,* Brookhaven National Laboratory; *S. Ismail-Beigi,* ***Eric Altman***, Yale University

Two-dimensional (2D) transition metal (TM) silicates have the potential to add magnetic, piezoelectric, and multiferroic functionalities to the toolkit of 2D layers used to develop new technologies. To date, these 2D TM silicates have been chemically bound to the growth substrate through oxygen atoms; the ability to weaken the interaction with the substrate to isolate the materials as single vdW layers is crucial for realizing their potential. Hydration or hydrogenation of the 2D TM silicate presents an ideal modification methodology to pacify the bonds to the substrate and create tailored interface properties and functionalities. Towards this end, here we report the interaction of Au- and Pd-supported 2D TM silicates with H_2O, H_2, and O_2. We employed a range of characterization tools to assess the materials before and after treatment with the probe molecules. Ambient pressure x-ray photoelectron spectroscopy (AP-XPS), ambient pressure infrared reflection absorption spectroscopy (AP-IRRAS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) in conjunction with first principles theory were utilized to assess surface morphology, interface characteristics, surface chemistry, and chemistry in in the confined spaces between the 2D TM silicate and metal support. The interaction of probe molecules with TM silicates on Pd(111) and Au(111) was studied over wide pressure (10^{-6}–1 mbar) and temperature (300–600 K) ranges. The data show that the dissociative adsorption of H_2 takes place to form OH bonds on the oxide surfaces under UHV conditions. When the pressure is increased to several mbar, the metal silicate surfaces are saturated with H atoms at 300 K. Exposure to H_2 at higher surface temperatures (≥ 600 K) reduces the TM silicate. Also, water dissociates readily on the metal silicate surfaces at 300 K. With an increase in H_2O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 mbar H_2O, molecular and dissociated water coexist (hydrogen bond OH/H_2O). In temperature-dependent studies, desorption of weakly bound water and surface dehydroxylation were observed with increasing temperature. Via AP-XPS combined with IRAS we study in detail the interaction of oxygen with the oxide surfaces, which shows that H_2-induced reduction can be reversed and the original structure restored. Our studies provide an effective avenue to achieve hydrated metal silicate layers and shed light on how to tune the chemical reactions of these overlayers by choosing suitable substrates.

3:00pm **SS+2D+AS-TuA-3 Metal Oxide and Metal Dichalcogenide 2D Nanocrystals: Structure, Adsorption and Catalytic Properties***, **Jeppe V. Lauritsen,*** Aarhus University, Denmark **INVITED**

Nanocrystals of two-dimensional materials may exhibit fascinating optical, electronic or chemical properties. In heterogeneous catalysis, the edge sites of some planar metal oxide and metal sulfide nanocrystals have been demonstrated be far more active than the majority sites exposed on basal planes. These observations have motivated us to obtain a better understanding of the edge site structure of 2D nanocrystals and try to establish the fundamental connection to their behavior in heterogeneous catalysis and electrocatalysis. I will discuss two examples showing how we investigated the structure and adsorption properties at the atomic scale by using scanning tunneling microscopy (STM) and photoemission spectroscopy techniques (XPS) on well-defined planar 2D nanocrystals supported on model substrates:

i. We used to atom-resolved STM images investigate edge reactivity of monolayer $CoOOH_x$ particles, widely considered as the active phase of cobalt-based catalysts in alkaline electrochemical water splitting. Water exposure experiments combined with atom-resolved STM imaging directly show an increased capacity to dissociate water on the edge sites, which is further substantiated by theoretical modelling [1]. Moreover, addition of Fe has strong promotional effect on the oxygen evolution. We have compared how the $CoOOH_x$ nanocrystals and chemical composition develops after the sample has been used as the working model electrode directly in a homebuilt *in situ* electrochemical cell attached to the STM chamber [2]. Our activity measurements confirm the expected increased oxygen evolution (OER) activity for Co-oxides mixed with Fe, which however depends in a highly non-linear way on the actual Fe content. Based on this information we found a model where the main effect of Fe doping in Co oxide is that of a structural edge stabilizer [3].

ii. MoS_2 nanocrystals are active catalysts in heteroatom extrusion from hydrocarbons (O, N, S) in oil and bio-oil processing (hydrotreating). Atom-resolved STM studies of MoS_2 nanocrystals as a supported model catalysts was used in combination with DFT analysis of molecule adsorption on MoS_2 edge to evidence an interesting new mechanism where adsorption of heteroatom-bearing hydrocarbons on a vacancy pushes neighboring S atoms aside. Thereby the adsorption event itself creates better catalytic active sites capable of adsorbing large hydrocarbons, explained the unusually wide selectivity of MoS_2 towards these reactions [4].

[1] J. Fester, et al., Nat. Comm **8**, 14169 (2017).

[2] Z. Sun, et al., Rev. Sci. Inst. **92**, 094101 (2021).

[3] Z. Sun, et al., ACS Nano **15**, 18226 (2021).

[4] N. Salazar, et al., Nat. Comm **11**, 4369 (2020).

4:20pm **SS+2D+AS-TuA-7 Intercalated $Cu_{2-x}O$ Thin Film Confined Underneath Hexagonal Boron Nitride***, **J. Trey Diulus**, Z. Novotny, N. Dongfang, N. Comini, J. Beckord, Y. Al-Hamdani,* University of Zurich, Switzerland*; M. Muntwiler,* Paul Scherrer Institute, Switzerland*; M. Hengsberger, M. Iannuzzi, J. Osterwalder,* University of Zurich, Switzerland

Confined catalysis has been achieved in zero and one dimensions using zeolites, metal-organic frameworks, and carbon nanotubes for optimized catalytic performance. Confinement can also be achieved in two dimensions by intercalation of reactants between solid layers. 2D materials grown on metal surfaces have become widely used model systems to study 2D-confined catalysis. Yet, numerous transition metals have been found to be more active in their oxidized form. Unfortunately, the growth of h-BN *via* chemical vapor deposition (CVD) has proven to be more difficult on metal oxides than on metals. Instead, a metal substrate underneath an h-BN monolayer can be oxidized *via* O_2 intercalation. Due to weak interactions between h-BN and Cu(111), the Cu(111) substrate is a prime candidate for intercalated oxidation, forming a thin oxide film (~3 Å) while the h-BN remains intact. Growth of h–BN on Cu(111) was achieved through CVD by borazine exposure in ultra-high vacuum at the In Situ Spectroscopy beamline at the Swiss Light Source (SLS). The surface structure, chemical composition, and uniformity of the as-grown h-BN/Cu(111) heterostructure were determined with low-energy electron diffraction, Auger electron spectroscopy, and X–ray photoelectron spectroscopy (XPS). Oxidation of the Cu(111) under h-BN *via* O_2 intercalation was executed by exposure to near-ambient partial pressures of O_2 (0.001 to 1 mbar) at temperatures ranging from 25 to 200 °C. Ambient pressure XPS and X-ray absorption spectroscopy were utilized at each temperature and pressure to determine the oxidation state of Cu and develop a recipe for preparing an ordered h–BN/$Cu_{2-x}O$/Cu(111) heterostructure. Further characterization of an ordered h–BN/$Cu_{2-x}O$/Cu(111) was obtained at the PEARL beamline at the SLS. Scanning tunneling microscopy (STM) provided atomic-resolution imaging of the sample held at 78 K, displaying a Cu_2O-like structure. STM further shows the oxidation of the Cu(111) substrate occurs *via* O intercalation at the h-BN grain boundaries. Density functional theory calculations, X-ray photoelectron diffraction experiments, and multiple-scattering simulations using the Electron Diffraction in Atomic Clusters code, provided further structural information, suggesting O atoms first adsorb to HCP-Cu sites on Cu(111), followed by the formation of a Cu_2O-like trilayer in between the substrate and h–BN. Ultimately, we fully characterize the structure and oxidation mechanism of a well-defined nano–reactor system that is ideally suited to study reactions in confined space. Furthermore, we propose this preparation method can be applied to more systems comprising of a 2D monolayer on a metal substrate.

4:40pm **SS+2D+AS-TuA-8 Imaging Surface Defects on MoS_2***, **Blake Birmingham,*** Baylor University

MoS_2 is an exciting hydrogen evolution reaction (HER) catalyst that exhibits promising activity in acidic media. However, the role of density and reactivity of defect sites to the HER performance of MoS_2 is currently unclear. Up to now, correlation of localized HER activity to atomic scale defects have been inferred via ex-situ measurements, where the macroscopic electrode activity is determined via bulk electrochemical techniques and correlated with the number of active sites that are measured separately via nanoscale surface imaging such as Scanning Tunneling Microscopy (STM) or Transmission Electron Microscopy.

In the presented experiment, the structural and chemical properties of bulk mineral MoS_2 catalyst during HER were monitored in-situ by electrochemical scanning tunneling microscopy (EC-STM). The nanoscale structure of the MoS_2 is correlated with its electrochemical activity in 0.5 M H_2SO_4(aq) electrolyte. Defects on the MoS_2 basal plane were atomically resolved before and after several rounds of cyclic voltammetry (CV) measuring the HER current vs applied potential against a carbon reference. Atomically resolved imaging of the same nanoscale area before and after HER does not show an increase in atomic defect site density after prolonged HER probed by many rounds of CVs. This indicates that new sulfur vacancies are either not produced during HER on MoS_2 basal plane or are produced and immediately occupied by hydrogen atoms. The surface was imaged near the HER onset potential, the evolution reaction was directly imaged as strong local tunneling instability. The tunneling destabilization effect is strongest near the nanoscale defect sites potentially due to local hydrogen gas bubbling.

5:00pm **SS+2D+AS-TuA-9 Modifying 2D Transition Metal Dichalcogenides (TMDs) by Incorporating Excess Transition Metals*, Matthias Batzill,*** University of South Florida **INVITED**

Crystal modifications in 2D materials can introduce new functionalities in these materials. Here we discuss compositional and structural crystal modifications in some transition metal dichalcogenides (TMDs). Specifically, we show that excess metals can be incorporated into the crystal structures of Mo-, and W- dichalcogenides and in PtTe2. In the former the excess metals result in the formation of metal rich mirror twin grain boundary networks, while in the latter a phase transition from PtTe2 to Pt-monotelluride can be induced. In this presentation we discuss the transformation mechanisms and the properties that arise from these compositional modifications.

5:40pm **SS+2D+AS-TuA-11 SSD Flash Poster Session: Oral Presentations***,*

5:40: SS-TuP-7 - Dr. Pierluigi Bilotto

5:43: SS-TuP-12 - Dr. Benjamen Reed

5:46: SS-TuP-13 - Mr. Xiao Zhao

5:49: SS-TuP-6 - Dr. J. Trey Diulus

5:52: SS-TuP-9 - Mr. Dustin Johnson

5:55: SS-TuP-18 - Aman Patel

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen**,* University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 $mAcm^{-2}$) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (*AMX_3*). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

References:

1. P. K. Nayak, S. Mahesh, H. J. Snaith, D. Cahen, *Nat. Rev. Mater.*, **2019**, *4*, 269-285.
2. H. Kaslasi, Y. Feldman, Y. Rakita, D. Cahen, G. Hodes,*Cryst. Growth Des*, **2020**, *20*, 4366-4374.
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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeM

Advances in Materials and Analysis in Heterogeneous Catalysis II

Moderators: Sanjaya Sennayake, Brookhaven National Laboratory, **Jason Weaver**, University of Florida

8:20am **HC+AS+SS-WeM-2 Development and Characterization of Highly Stable ALD Coated Catalysts for Dehydrogenation of Light Alkanes*, Jonathan Travis,*** *J. Burger, A. Dameron,* Forge Nano

Catalysts are critical materials for enabling many modern industrial chemical processes, such as the dehydrogenation of light alkanes to produce “on purpose” alkenes. Catalyst deactivation costs the chemical industry billions of dollars. One of the major mechanisms of deactivation is metal sintering during high temperature regeneration. Atomic Layer Deposition (ALD) overcoating has previously been demonstrated to stabilize catalyst materials against sintering and deactivation, as well as improve selectivity in certain cases. In this study the properties and performance of 0.1% Pt/Al_2O_3 catalysts are investigated as a function of surface modification via ALD Al_2O_3 coatings. The catalysts are characterized in Forge Nano’s in-house catalyst characterization laboratory. Physical characterization is performed using various techniques including moisture analysis, BET Surface Area, Porosimetry, TGA, CO Chemisorption, ICP-MS, and Temperature Programmed Reduction, Desorption, and Oxidation. Performance is characterized using propane dehydrogenation under a variety of conditions. This talk will present the effects of Forge Nano’s ALD Al_2O_3 coating on the properties and performance of the 0.1% Pt/Al_2O_3 catalysts.

8:40am **HC+AS+SS-WeM-3 Combining Theory with Ambient Pressure XPS to Reveal Chemistry at Interfaces Under *In Situ* and *Operando* Conditions*, Ethan Crumlin,*** Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of essential interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and converted. This talk will focus on using ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical-specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various *in situ*/*operando* features such as heating to temperatures > 500 °C, pressures greater than 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials support the ability to collect XPS data of actual electrochemical devices while it's operating in near ambient pressures. This talk will share our efforts to combine theory and APXPS to understand the chemistry at solid/gas and solid/liquid interfaces under *in situ* and *operando* conditions. At the solid/gas interface, we will share our work to understand how carbon dioxide interacts with copper and silver surfaces using APXPS and theory to generate observables that we could experimentally verify. Separately I will introduce our strategy to introduce a chemical reaction network to generate spectra of water interacting with a silver surface that directly resembled our APXPS measurements. At the solid/liquid interface, the combination of theory and APXPS revealed how stable magnesium electrodes and stable diglyme electrolytes could be unstable when in contact with each other. In addition, it facilitated the prediction of the sensitivity for probing interfacial chemical species at a solid/liquid interface. To further advance these directions and synergy for combining theory and experiments, I will show our recent progress in creating an interfacial Digital Twin that we hope will rapidly accelerate our understanding of interfacial chemistry.

9:20am **HC+AS+SS-WeM-5 The Electrochemical Interface as a Reactive Environment to Resynthesize Electrode Surface Chemistry Using the Dissolution-Redeposition Dynamics*, Feng Lin,*** Virginia Tech **INVITED**

The solid-liquid electrochemical interface offers a two-dimensional environment for geometrically confined interfacial reactions to tailor electrode surface chemistry under operating conditions. Herein, we demonstrate that the dissolution and redeposition kinetics of transition metal cations, a ubiquitous phenomenon at the electrochemical interface, can be manipulated to regulate the chemical composition and crystal structure of the electrode surface as well as the overall electrochemical performance. Foreign cations, either added as electrolyte additives or dissolved from surface coatings, can rapidly participate in the electrode dissolution-redeposition process, and facilitate the establishment of the dissolution-redeposition equilibrium. We will present scientific case studies in electrocatalysis. Our work expands the control over the electrochemical reactions at the solid-liquid interface and provides new insights into interfacial studies in electrochemistry, and surface science.

11:00am **HC+AS+SS-WeM-10 Ambient Pressure Spectroscopy of Catalytic Porous Nanofilms***, C. Eads,* MAX IV Laboratory, Sweden*; T. Hu, S. Tenney,* ***Ashley Head,*** Brookhaven National Laboratory **INVITED**

Porous materials offer an opportunity for catalysis in confined spaces. By spatially confining chemistry, reaction dynamics and selectivity can change in unknown ways. Two examples will be discussed, including Pt nanoparticles embedded in a thin film of the metal-organic framework UiO-66(NH_2) and a two-dimensional silicate on Pd(111). Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used to characterize the electronic structure of the Pt-embedded metal-organic framework. CO oxidation and CO_2 reduction have been followed with IR spectroscopy and mass spectrometry. In a second system, the space between a two-dimensional silicate and a Pd(111) surface promotes more CO oxidation than a bare Pd surface. IR spectroscopy shows that the silicate film changes the surface adsorbates, resulting in increased CO_2 formation, as confirmed with mass spectrometry. These results will help enable the rational design of materials to spatially confine reactions in a desired way.

11:40am **HC+AS+SS-WeM-12 Catalytic Oxidation of Methane on IrO_2(110) Films*, Jovenal Jamir,*** *R. Martin,* University of Florida*; M. Kim,* Yeungnam University , Republic of Korea*; C. Lee, V. Mehar,* University of Florida*; A. Asthagiri,* The Ohio State University*; J. Weaver,* University of Florida

In recent years, IrO_2(110) films have gained increasing interest for their ability to strongly adsorb light alkanes and cleave C-H bonds below room temperature. Our group has shown, via ultrahigh vacuum (UHV) temperature programmed reaction spectroscopy (TPRS) experiments, that initial methane activation occurs at temperatures as low as 100 K and leads to the desorption of CO, CO_2 and H_2O above 400 K. The large temperature range over which partially oxidized methane-derived species exist, along with the facile nature of C-H bond cleavage motivates further study of methane oxidation under catalytically relevant conditions. In this talk I will discuss recent kinetic studies performed in a batch reactor to investigate the catalytic oxidation of CH_4 on IrO_2(110) films at gas pressures near 1 Torr as well as results of ambient pressure x-ray photoelectron spectroscopy (AP-XPS) measurements and molecular simulations. We find that IrO_2(110) is highly active for the catalytic combustion of CH_4 at moderate temperatures (500-650 K), with comparable activities to PdO catalysts. Our results further show that catalytic CH_4 oxidation is mildly activated on IrO_2(110) and that the catalytic rates depend slightly inversely on the O_2 partial pressure, suggesting that the dissociative chemisorption of O_2 is more efficient than CH_4 activation and acts to blocks CH_4 adsorption sites. AP-XPS measurements reveal that high coverages of OH groups and CH_yO_2 species form on IrO_2(110) during CH_4 oxidation and that O-rich IrO_2(110) surfaces are maintained even under highly CH_4-rich conditions (up to 95% CH_4), consistent with efficient O_2 adsorption and site competition with CH_4. Finally, I will discuss how we have combined our AP-XPS results with catalytic rate measurements to develop first principles, microkinetic models for methane oxidation over IrO_2(110). Of particular significance is that earlier models did not consider surface CH_yO_2 species. Our AP-XPS results thus inspired efforts to identify additional reactions and determine the roles that various adsorbed species play during catalytic CH_4 oxidation on IrO_2(110). Our findings highlight how operando surface spectroscopy can provide key guidance for understanding catalytic reaction mechanisms and developing accurate kinetic models.

12:00pm **HC+AS+SS-WeM-13 HC Graduate Student Finalist Talk: *Operando* Observation of Metal Encapsulation Causing Strong Metal-Support Interaction at the Pt-Co_3O_4 Interface***, **Daeho Kim,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; D. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Song,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; B. Jeong,* Korea Basic Science Institute (KBSI), Republic of Korea*; Y. Jung,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Noble metal nanoparticles (NPs) supported on metal oxide (e.g., Co_3O_4, NiO, TiO_2, CeO_2, and Fe_2O_3) have been commonly utilized as a heterogeneous catalyst for improving catalytic performance and modifying the reaction pathway of various catalytic reactions, such as CO oxidation, CO_2 hydrogenation, and Fischer-Tropsch synthesis. The unique interaction at the interface of the metal NP and oxide, which is known as the strong metal-support interaction (SMSI), gives synergistic enhancement to the catalytic activity. Hence, a fundamental understanding of SMSI with bridging pressure and material gaps using operando surface characterization is necessary for developing high-performance heterogeneous catalysts.

Herein, we show the direct evidence of SMSI at the interface of Pt NP and Co_3O_4, utilizing operando surface analysis. The Pt-Co_3O_4 interfaces were prepared as powder catalysts using colloidal Pt NPs embedded on the mesoporous Co_3O_4. The two-dimensional model system is also constructed on Co_3O_4–coated Si wafer via a Langmuir-Blodgett trough to bridge the material gap. The surface of prepared Pt-Co_3O_4 is comprehensively characterized under dynamic conditions: a reducing environment (H_2 or CO) and a catalytic reaction environment (CO + O_2). Combining computational calculation and the operando surface characterizations using ambient pressure X-ray photoelectron spectroscopy, environmental transmission electron microscopy, and diffuse reflectance infrared Fourier-transform spectroscopy, we suggest that the interface between Pt NPs and the thin oxide overlayer is a key state of the SMSI enhancing the catalytic activity.

Surface Science Division
Room 319 - Session SS2+AS+HC-WeM
Nanoparticle Surfaces

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

9:40am **SS2+AS+HC-WeM-6 Understanding the Growth of Sn and Pt-Sn Clusters on Titania and Carbon Surfaces***, S. Beniwal,* University of South Carolina*; W. Chai,* University of Texas at Austin*; M. Qiao, P. Kasala,* University of South Carolina*; K. Shin, G. Henkelman,* University of Texas at Austin*;* ***Donna Chen,*** University of South Carolina

Supported Pt-Sn bimetallic clusters have applications in number of catalytic processes, including dehydrogenation of alkanes and selective hydrogenation of unsaturated aldehydes. In these reactions, the presence of Sn is known to promote the desired selectivity of the Pt-based catalyst. However, the chemical activity the supported Pt-Sn catalysts is dependent on the Sn oxidation state and the nature of Sn interaction with the support, as well as dispersion. Sn and Pt-Sn clusters have been vapor-deposited on TiO_2(110) and highly oriented pyrolytic graphite (HOPG) and studied by scanning tunneling microscopy, X-ray photoelectron spectroscopy, and low energy ion scattering. Deposition of Sn on titania results in the formation of small, uniformly sized clusters with SnO_x at the cluster-support interface and reduction of the titania support. Subsequent deposition of Pt produces exclusively bimetallic clusters, and Sn diffuses away from cluster-support, resulting in a decrease in SnO_x and Sn-rich cluster surfaces. Density functional theory (DFT) calculations demonstrate that M-TiO_2 bonding is favored over M-M bonding for M=Sn, unlike for transition metals such as M=Pt, Au, Ni, and Co. Furthermore, the substantial charge transfer from Sn to TiO_2 leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late transition metals. DFT studies also confirm that addition of Pt to a Sn cluster results in strong Pt-Sn bond formation and diminished Sn-O interactions. In the case of Sn deposition on HOPG, the clusters are surprisingly small given that Sn does not interact strongly with the support, whereas other metals such as Pt, Re and Pd readily diffuse to form large clusters that aggregate at step edges. DFT investigations show that Sn is unique in that the per atom binding energy of Sn in small clusters (<15 atoms) is as low as 0.14 eV/atom compared to Sn atoms in the bulk; for Pd, Pt, and Re, the binding energy is 0.9-1.9 eV/atom. Therefore, it is thermodynamically favorable for Sn to form small clusters and for other metals to form large clusters.

11:00am **SS2+AS+HC-WeM-10 Single Nanoparticle Surface Chemistry: Structure-Reactivity Relationships, Evolution During Reactions, and an Approach to Ultra-High Temperature Surface Chemistry***, C. Lau, A. Friese, D. Rodriguez,* ***Scott Anderson,*** University of Utah

Nanoparticles (NPs) are inherently heterogeneous, with variations in size, shape, and distributions of reactive sites. This talk will explore the kinetics for oxidative etching of *individual* carbon and silicon NPs, tracking changes in reactivity as the NP structure evolves under reaction conditions.

Examples of O_2 oxidation of typical carbon black and graphene oxide NPs is shown in the figure, which shows the NP mass vs. time at 1200 K under inert (unshaded background) and oxidizing conditions (cyan background). The lower frames show how EE_{O2}(the etching efficiency in terms of Da of mass lost *per* O_2 collision) varies with the NP mass. Oxidative etching of carbon NPs varies significantly between NPs from different feedstocks, but there are also variations between NPs from the same feedstock, reflecting variations in the distributions of surface sites. Furthermore, the reactivity of individual NPs evolves non-monotonically in time as the NPs etch, with rate fluctuations of up to 5 orders of magnitude. Eventually, all carbon NPs become nearly inert to O_2, signaling that the surface layer(s) have transformed to multiwall fullerene-like structures.

For silicon NPs, we are able to study oxidation over a temperature range from 1200 to 2500 K, spanning the bulk T_{melt} of both silicon and silica. Etching involves several interacting processes that depend differently on temperature and time, thus etching of silicon-based NPs can have quite complex time dependence. For example, at temperatures (e.g. 1200 K) well below the silicon melting point (T_{melt} = 1683 K), the etching mass loss rate is initially low, accelerating as etching progresses, then eventually dropping several orders of magnitude to ~zero as the NP surface grows a passivating silica layer. At temperatures closer to the melting point (e.g. 1500 K), the oxidative mass loss rate starts high and remains high as the NP loses 15 – 30% of its initial mass, then abruptly drops to near zero as the surface passivates. For temperatures above T_{melt}, the etch rate begins to decrease immediately upon O_2 exposure, but it never drops to zero, i.e., the NP surface never passivates.

One of the features of this method is that the upper temperature possible is limited only by the sublimation rate of the particle's material. Thus for Si, it is straightforward to examine temperatures well above T_{melt}. For ultra-high temperature ceramic materials, it is possible to study surface chemistry at temperatures to well above 3000 K. Oxidation of HfC ($T_{melt}\approx$ 4200 K), will be used to illustrate this capability.

11:20am **SS2+AS+HC-WeM-11 Oxidation of Size-Selected Ag Clusters on Graphene: Bulk Motifs and Electronic Anomalies at sub-Nanoscale***, F. Loi,* University of Trieste, Italy*; M. Pozzo,* University College London, UK*;* ***Luca Bignardi,*** *L. Sbuelz,* University of Trieste, Italy*; P. Lacovig, E. Tosi, S. Lizzit,* Elettra Sincrotrone Trieste, Italy*; A. Kartouzian, U. Heiz,* Technical University Munich, Germany*; R. Larciprete,* Institute for complex systems - CNR, Italy*; D. Alfè,* University College London, UK*; A. Baraldi,* University of Trieste, Italy

The evolution of the aggregation of condensed matter from single atoms to three-dimensional structures represents an crucial topic in nanoscience since it contains essential information to achieve tailor-made growth of nanostructured materials. Such issue is particularly important in the case of the formation of nano-oxides, which have strong potentialities in heterogeneous catalysis reactions. In this respect, we investigated the oxidation of an Ag nanocluster composed of 11 atoms supported on epitaxial graphene on Ru(0001), combining synchrotron-based core-level photoelectron spectroscopy and *ab initio* DFT calculations. Our analysis indicated that a single Ag_{11} cluster can bond with up to 12 O atoms. Moreover, we evidenced that the Ag-O bonds in the nanoclusters include contribution from the Ag 4d states, with a remarkable difference with the case of Ag single crystal surfaces, for which only Ag 5s states are involved. The oxidized $Ag_{11}O_{12}$ nanocluster is indeed more similar to a bulk oxide rather than to an oxidized surface, as it reaches a final hybrid structure formed of d^{10} Ag(I) and d^{8} Ag(III) ions which strongly resembles that of AgO bulk oxide. Furthermore, we found that the Ag 3d core level in the Ag_{11} nanoclusters is dominated by initial state effects and has a unique behavior when increasing the oxygen density. This anomaly seems to be related to the dimensionality of the nanocluster and provides an excellent example of the differences that sub-nanometer atomic aggregates of a material show with respect to the bulk and surface counterparts.

11:40am **SS2+AS+HC-WeM-12 Precision Engineering of Metal Nanoparticle Surfaces for Fundamental Studies of Catalytic Reactivity***, **Michelle Personick**,* Wesleyan University **INVITED**

Understanding fundamental structure-activity relationships in catalysis is key to enabling the directed design of improved catalytic materials, but the surfaces of working catalysts are complex. The use of precisely defined nanomaterials provides a powerful tool for facilitating insights into active site structure and reaction mechanisms. Such materials also enable testing and validation of insights from fundamental experimental and computational surface science under catalytic operating conditions. However, synthesizing nanomaterials with the precise surface structures and compositions necessary to test specific hypotheses is a significant challenge, and creative new approaches to materials synthesis are required—particularly for bimetallic materials. This talk will highlight the use of large (~75 nm), well-defined metal nanoparticles as model surfaces to test predictions from computational surface science. In addition, it will describe materials-generalizable synthetic tools developed by our research group for controlling metal nanoparticle shape, surface structure, defect structure, and composition, with an emphasis on dilute bimetallic nanoparticles. Halide-assisted metal ion reduction enables the controlled co-reduction of metals with dissimilar reactivity (Au/Pd, Pd/Cu, Au/Ag), while differentially tuning the relative rates of reduction for each metal to define the shape and surface composition of the material. Plasmon-assisted metal ion reduction takes advantage of the light-responsive properties of materials like Ag to enable (1) the directed deposition of catalytically active but poorly plasmonic metals such as Pt, and (2) the reconfiguration of monometallic Ag materials to modify defect structure while retaining the same surface structure and adsorbates. Together with other techniques developed in our research group, these tools provide a platform for the precision engineering of catalytic metal nanomaterials.

Applied Surface Science Division
Room 320 - Session AS+CA+HC+LS-WeA

Shining a Light on Surface Chemical Metrology: In Memory of Martin Seah

Moderators: Donald Baer, Pacific Northwest National Laboratory, **Alexander Shard**, National Physical Laboratory, UK

2:20pm **AS+CA+HC+LS-WeA-1 Metrology Lights the Way for Advances in Metabolic Imaging at the Single-cell Scale*, Ian Gilmore,*** National Physical Laboratory, UK **INVITED**

The international community recently paid homage to Martin Seah in a Special Issue of Surface Interface Analysis [1] with reminiscences, biographical accounts of his considerable achievements, reviews and research articles. The collection takes its title "Shining a light on surface chemical analysis" from Martin's research career of over 5 decades dedicated to guiding the community to make better measurements in traditional and emerging areas of surface chemical analysis. Where there was darkness, he brought light. Here, we begin with a retrospective look at Martin's considerable achievements in XPS, AES, SIMS, AFM and leadership in International Standardisation.

Martin was never one for too much retrospection though and was always full of energy and enthusiasm to tackle the issues of tomorrow. We therefore show how by using Martin's methodology that metrology is lighting the way for metabolic imaging at the single-cell scale, which is of critical importance in the development of new pharmaceuticals, understanding tumour heterogeneity and fundamental biological studies to understand metabolic rewiring in diseases.

References

[1] Gilmore, I.S. (2022), Martin P Seah MBE—Shining a light on surface chemical analysis. Surf Interface Anal, 54: 282-284. https://doi.org/10.1002/sia.7071

3:00pm **AS+CA+HC+LS-WeA-3 Two-Point Calibration Method for Quantifying Organic Binary Mixtures Using SIMS in the Presence of Matrix Effects*, Alexander Shard,*** National Physical Laboratory, U.K.*; A. Miisho,* Kobelco, Japan*; J. Vorng, R. Havelund, I. Gilmore,* National Physical Laboratory, U.K.*; S. Aoyagi,* Seikei University, Japan

Quantification of composition for organic mixtures is required in the analyses of technological materials from organic electronics to drug delivery systems. The molecular specificity of secondary ion mass spectrometry provides an unparalleled ability to distinguish organic materials, however it is difficult to use for quantitative analysis. In a few cases, there is a linear dependence between the composition, expressed as a ratio of component volumes, and the secondary ion intensities, expressed as a ratio of intensities of ions from each component. However, this ideal relationship fails in the presence of matrix effects and linearity is observed only over small compositional ranges, particularly in the dilute limits. We present an empirical method which introduces a power law dependence between the intensity ratio and the volume fraction ratio. A physical model of the organic matrix effect is employed to test the limits of the method and a mixed system of 3,3'-bis(9-carbazolyl) biphenyl and tris(2-phenylpyridinato)iridium(III) is used to demonstrate the method. In practice, we describe a two-point calibration, which determines both the exponent in the power law and the sensitivity factor for the conversion of ion intensity ratio into volume fraction ratio. We demonstrate that the two-point method significantly improves the accuracy of quantification compared to a one-point, linear calibration and is valid over a wide compositional range. Since the method enables the use of clearly identifiable secondary ions for quantitative purposes and mitigates commonly observed matrix effects in organic materials, the two-point calibration method could be of significant benefit to SIMS analysts.

3:20pm **AS+CA+HC+LS-WeA-4 OrbiSIMS Metrology: Optimization of Inorganic Depth Profiling using Ge and Sb Delta-layer Samples***, Y. Zhou,* National Physical Laboratory, UK*; A. Franquet, V. Spampinato,* IMEC, Belgium*; A. Pirkl,* IONTOF GmbH, Germany*; W. Vandervorst, P. Van Der Heide,* IMEC, Belgium*; **Ian Gilmore,*** National Physical Laboratory, UK

In 2017, NPL introduced the 3D OrbiSIMS instrument [1] for sub-cellular resolution molecular imaging with high-mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). Since then, IONTOF installed multiple Hybrid SIMS systems around the world with a growing range of applications, largely in, but not limited to, the life-sciences.[2,3] The dual ToF-MS and Orbitrap-MS analyzers combined with Bi liquid metal, gas cluster, and low energy $O_2^+$and Cs^+ ion beams provide a highly versatile platform for materials science studies.

Since the Orbitrap-MS is designed to operate with a continuous ion source, the instrument is well configured to take advantage of single ion beam depth profiling approaches. For example, Sul et al[4] recently demonstrated the ability to sputter depth profile a blue phosphorescent OLED device using GCIB sputtering with Orbitrap-MS. Similarly, Spampinato used the high-mass resolving power of the Orbitrap-MS to study thin EUV photoresist films where ToF-SIMS suffered from severe molecular interferences. [5] Moreover, there is growing interest in the application of the OrbiSIMS to inorganic semiconductors. Franquet et al[6] recently showed how the high mass resolution of the Orbitrap-MS analyzer combined with 2 keV Cs^+ sputtering enabled the composition of SiGe architectures down to < 20 nm to be determined with improved accuracy using the Self Focusing SIMS methodology.[6]

In this study, we use a sample consisting of 8 Ge delta-layers with a spacing of 4.8 nm in a silicon matrix. The thickness of each delta-layer is ~0.2 nm with a concentration of below 1 atom%. A second sample consisting of 5 Sb delta-layers with a spacing of 10 nm in a silicon matrix was also used. A sputter gun using either O_2^+or Cs^+ between 1 keV and 2 keV was used for both sputtering and analysis with Orbitrap-MS detection. The optimization of instrument parameters including sputter rate, injection time and sputter beam energy on the depth resolution (λ_g, λ_d and Gaussian broadening)[7]will be discussed.

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4. S. Sul, G. Trindade, J. Kim, et al, https://www.researchsquare.com/article/rs-1279729/v1 (2022).

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4:20pm **AS+CA+HC+LS-WeA-7 Complementary Perspectives on the Impacts of Martin Seah on Surface Analysis*, Don Baer,*** Pacific Northwest National Laboratory **INVITED**

Throughout his more than four decade career Dr. Martin Seah had a major impact on quantitative surface analysis and the surface analysis community. There were many facets to his activities, interactions, and leadership and most of those who interacted with him knew only a portion of his many contributions. This talk will describe ways that he impacted my career and some of the activities that may have been less visible to many in the surface analysis community. Accurate quantitative surface analysis was a theme throughout his career. My introduction to his work was associated with measurements of the segregation of trace elements to the grain boundaries of metals and metal alloys.In the 1970s understanding of the challenges to quantitative analysis of electron spectroscopy was evolving and results were often inconsistent and sometimes a source controversy. Work by Seah and Hondros was important to put these measurements on a sound foundation. An important trait of Martin's work was his ability to identify needs or information gaps and to proceed to fill them.There are many examples of this, including application of XPS to measure very thin oxide films on silicon wafers, simple models of electron mean free path lengths, models for understanding sputtering rates of cluster ion sources and the development of consistent terminology for surface methods and analysis. Martin made significant and enjoyable efforts to communicate information to the community and offered encouragement to other researchers in a variety of ways.Although his presentations seemed to be spontaneous and often full of humor, they were always well thought out and delivered clear and important messages. In viewing one of my presentations the year of his death, he made many complementary remarks in email correspondence, but chided me for having too much information on my closing slide.He said that it was important to have a simple clear final message for each talk. A portion of his influence and success was due to many delightful professional and informal social interactions.When he liked a presentation, he would offer a simple "well done" and I very much valued such comments when I received them.At an American Chemical Society Meeting in New York City we went to the half price theatre ticket booth and chose to attend not a Broadway musical but a delightful Arthur Miller play with almost no audience.

5:00pm **AS+CA+HC+LS-WeA-9 The 'Crypto-Electron' Question: XPS of Tribo-electrified Insulators*, Hagai Cohen,*** Perlman bdg., The Weizmann Institute, Israel

Recent experiments on tribo-electrification have raised fundamental questions on the role of electrostatic charge in chemical and physical surface activity. Cryptolectrons were claimed to be created and, subsequently, be exploited to establish 'single-electrode electrochemistry'. However, our XPS study of this problem reveals methodological issues that were not taken into account. I will show that XPS proposes an interesting template for studies of various processes under controlled surface charge conditions, with which limiting factors on the magnitude of electrostatic surface fields can be extracted. How would a cryptoelectron, if existing, look like and can XPS imitate this creature to some extent – these questions and related ones will be discussed.

5:20pm **AS+CA+HC+LS-WeA-10 Effects, in XPS, on Composition Determination Using Different Background Removal Procedures: Single Crystal Fe_2O_3 as an Example*, Christopher R. Brundle,*** C R Brundle and Associates*; B. Crist,* xpsdata*; P. Bagus,* University of North Texas

Precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult, even for homogenous materials. Normalizations for σ and λ are required, but the procedures are by now well understood. The accuracy of removing a background to establish the intrinsic spectrum is on less secure ground. There are several approaches, and implementation requires adjustment of parameters either manually, or automatically by the software used. The situation is at its most unsure when an XPS core level "peak" consists of overlapping structure spread over a wide (up to several 10's ev) BE range, such as with Fe 2p (multiplet splitting; shake structure) and O1s (shake) in Fe_2O_3 (1). The situation is similar for many other transition metal compounds. We examine, for a hematite single crystal, Tougaard and Shirley based background removals. Our conclusion is that the high BE endpoint, ie. where the person taking, or analyzing, the data sets the background to meet the experimental spectrum (implying there is no further intrinsic signal beyond that BE) is critical for high composition accuracy. Obviously, theory input on where intrinsic substructure ends helps to establish what is a reasonable endpoint (1). It is quite possible to adjust endpoints (Fe2p and O1s) to return the "expected" answer, 40% atomic Fe, but this is arbitrary, and, of course, assumes 100% accuracy of the relative σ and relative λ in addition to assuming a) that the Transmission Function, TF, of the instrument has been accurately calibrated, and b) that a small signal from surface OH is properly accounted for. So, in this presentation we are more concerned with the *range in composition* returned by each method (and variations within each method), rather than absolute values, when different, but plausible, endpoints are used. We also find that results differ using high energy resolution and low resolution. The two effects together amount to a ~4% variation in determined Fe %age for Tougaard and ~6% for Shirley. We stress that this work represents a practical approach, using the particular versions of the Tougaard and Shirley software available with the instrument involved, and no sample treatment within the instrument, which we believe is the way most practical XPS analyses are actually performed. Finally, we discuss the reasons for the differences observed and examine other possible procedures.

1) Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3, Paul S. Bagus, Connie J. Nelin, C. R. Brundle, B. Vincent Crist, N. Lahiri, and Kevin M. Rosso, PCCP 2022 and references therein.

5:40pm **AS+CA+HC+LS-WeA-11 XPSOasis.org: the XPS Peak-Fitting Network*, Alberto Herrera-Gomez,*** CINVESTAV, Mexico*; D. Herrera-Rendon, E. Aguilar-Diaz,* RDATAA, Mexico

The XPSOasis Web platform aims to make available to the XPS community, free of charge, tools that facilitate communication between XPS users; this includes discussion forums, peak-fitting databases (one for each core-level), dynamic communication between users, and free data analysis software. The web platform allows users of different fitting software to easily upload posts to ask questions with images of the fitting that concern them. To answer the questions, the posts contain the data, allowing knowledgeable users to download and work on the recommendations.Novice users can consult expert users in direct conversations. Technical discussions on the analysis of XPS data can also be held.

To hook expert (and non-expert) users, the participation is rewarded with *Spicer* points, which are accumulated through *likes* in their posts (given by other users) and when one of their posts reaches the peak-fitting data base (which is a decision of the corresponding moderator).Categories are defined in terms of the points.User belonging to certain categories can compete to become moderators of a certain core-level forum and database.They could also offer courses.Another advantage of having posts in the database is that they become the norm and could be cited.

The usefulness of XPSOasis.org is a function on the availability of peak-fitting parameters for each core-level for each element under a variety of chemical environments.Since it is a user-based platform, it becomes more useful as the number of users posts increases.This is a possible solution (which will, in fact, be provided by the XPS community itself) for the erroneous XPS analyses all too common in the scientific literature.

6:00pm **AS+CA+HC+LS-WeA-12 ASSD Peter Sherwood Mid-Career Award Talk: Advancing X-ray Photoelectron Spectroscopy (XPS) Methodologies for Materials Research*, Mark Biesinger*[1]*,*** Surface Science Western, Canada

INVITED

Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems [1,2,3]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots [4,5]. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [5], have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications.

An overview of these curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.A recent assessment of available charge corrections procedures for insulating samples will also be shown [6].

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1. M.C. Biesinger, et al., *Surf. Interface Anal.***41** (2009) 324.

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4. J.L. Bourque, M.C. Biesinger, K.M. Baines, *Dalton Transactions***45** (2016) 7678.

5. M.C. Biesinger, *Surf. Interface Anal.***49** (2017) 1325.

6. M.C. Biesinger*, Appl. Surf. Sci*. **597** (2022) 15381.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeA

Bridging Gaps II: Single Atom Alloys and Desirable Defects

Moderators: Rachel Farber, University of Chicago, **Gareth Parkinson**, TU Wien, Austria

3:00pm **HC+AS+SS-WeA-3 Atomic-Scale Structure-Function Relationships of Pt-based Copper Oxide Single-Atom Catalysts*, Audrey Dannar,*** *A. Schilling, G. Giannakakis, A. Therrien, E. Sykes,* Tufts University

Single-atom catalysts comprised of isolated metal atoms anchored on oxide supports have recently gained considerable attention for their potential to

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[1] **ASSD Peter Sherwood Award**

improve the activity and or selectivity of important industrial reactions. We have previously shown that single Pt atoms on a copper oxide thin-film are able to perform low-temperature CO oxidation without sintering, a common deactivation mechanism of single-atom catalysts. Using a combination of scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopy, and temperature programmed desorption we elucidated the atomic-scale surface structure of these model catalysts and related that structure to catalytic function. We found that Pt atoms have a preferred binding site on the oxide surface and that they can oxidize CO, but not H_2. These fundamental surface results were leveraged in the design of nanoparticle analogs that were active and selective for the preferential oxidation of CO. In order to extend this approach to bulk oxides we have begun characterizing the 111 facet of a Cu_2O single-crystal which better mimics the Cu_2O particles present in high surface area catalysts. Scanning tunneling microscopy images of the Cu_2O(111) surface reveal atomic-scale structures that may be responsible for the reactivity observed in real catalysts. Low-energy electron diffraction patterns reveal reconstructions in the model catalyst surface induced by exposure to reducing or oxidizing conditions, which is important in terms of how the active sites, and their coordination to the oxide support evolve under relevant reaction conditions. Taken together, our thin-film and bulk copper oxide surfaces decorated with isolated Pt atoms provide useful model systems with which to parse out atomic-scale structure-function relationships that inform the rational design of novel catalysts.

4:20pm **HC+AS+SS-WeA-7 Comparison Study of Several Transition Metals on Two Different TiO_2 Model Supports: Anatase TiO_2 (101) and Rutile TiO_2 (110)**, ***Lena Puntscher***, *K. Daninger, P. Sombut,* TU Wien, Austria; *M. Meier,* University of Vienna, Austria; *M. Schmid,* TU Wien, Austria; *C. Franchini,* Alma Mater Studiorum, Università di Bologna, Bologna, Italy; *U. Diebold, G. Parkinson,* TU Wien, Austria

Single-atom catalysis (SAC) offers an opportunity to minimize the amount of precious catalyst material required for traditional heterogeneous catalysis and to "heterogenize" reactions presently requiring homogeneous catalysis; this would eliminate the problem of separating catalyst and product, while retaining the excellent selectivity and activity of homogeneous catalysts [1].

Unravelling how metal atoms bind to oxide supports is crucial for a better understanding of the SAC´s catalytic properties. Using STM and XPS, we compare the adsorption geometry and stability of several transition metals on TiO_2 model supports: anatase TiO_2(101) and rutile TiO_2(110) [2] and the influence of water on the dispersion of these systems.

This study points out the importance of metal-support interaction and the surprisingly different behaviour of the transition metals Pt, Rh, Ir and Ni on TiO_2 model supports.

1. Parkinson, G.S., *Single-atom catalysis: how structure influences catalytic performance.* Catalysis Letters, 2019. **149**(5): p. 1137-1146.
2. Sombut, P., et al., *Role of Polarons in Single-Atom Catalysts: Case Study of Me_1 [Au_1, Pt_1, and Rh_1] on TiO_2 (110).* arXiv preprint arXiv:2204.06991, 2022.

4:40pm **HC+AS+SS-WeA-8 Boron Effect Improves Catalytic Performance on Supported Pt/SiO_2 Catalysts for Dry Reforming of Methane at Reduced Temperatures**, ***Carly Byron***, University of Delaware; *M. Ferrandon, A. Kropf,* Argonne National Laboratory; *S. Bai,* University of Delaware; *M. Delferro,* Argonne National Laboratory; *A. Teplyakov,* University of Delaware

Metal nanoparticles supported on metal oxides are studied as catalysts for a variety of applications, most notably catalytic hydrocarbon reforming reactions. Platinum has shown to be a highly active catalyst for the dry reforming of methane (DRM), which converts CO_2 and CH_4 into "synthesis gas", which can be further processed to produce biofuel. However, the DRM process requires further optimization before large scale use. Our prior studies have shown that boron has a positive effect on platinum/silica catalyst for butane dehydrogenation, due to the reduction in carbon contaminant (coke) on the surface and migration of carbon deposit away from platinum active sites. Based on these findings, Pt/B/SiO_2 catalysts were prepared for DRM catalysis and compared with Pt/SiO_2 catalysts without boron promotion. Both catalysts had similar concentrations of platinum, but the catalytic activity after 14 hours for boron-containing catalyst was drastically improved, resulting in nearly 100% CO_2 conversion compared to 12% without boron. The reacted catalysts were investigated with synchrotron x-ray adsorption spectroscopy (XAS), transmission electron microscopy (TEM), x-ray electron spectroscopy (XPS), and Raman spectroscopy to identify the deactivating factor. It was determined that neither sintering nor coking was a significant factor in Pt/SiO_2 catalyst deactivation, instead that platinum and boron interact electronically to optimize DRM catalysis, which results in high activity at relatively low DRM operating temperatures.

5:00pm **HC+AS+SS-WeA-9 Facet Dependence of RhCu Single-Atom Alloy Structure and Reactivity**, ***Yicheng Wang***, *R. Hannagan,* Tufts University; *J. Schumann, M. Stamatakis,* University College London, UK; *C. Sykes,* Tufts University, UK

Direct propane dehydrogenation is a promising way to address the current propene shortage. RhCu single-atom alloys (SAAs), predicted by first-principal calculations, have recently been demonstrated to be efficient propane dehydrogenation catalysts. While RhCu model catalysts have been conducted on the (111) facet of Cu to understand the C-H activation mechanism, other facets have not been explored which is important fundamental information needed to bridge the structure gap between model catalyst and nanoparticle studies. In order to better understand the effect of the more open (100) facet, we investigated the RhCu(100) SAA surface using a combination of scanning tunneling microscopy (STM), temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT). Our STM results reveal a striking difference between the alloying mechanism of Rh atoms in Cu(111) versus Cu(100) surface facets.Unlike RhCu(111) where Rh atoms tend to form dense brim in the regions above the step edges, homogeneously dispersed Rh atoms can be observed across the whole Cu(100) surface. DFT modeling indicates that the starkly different Rh distribution can be attributed to the different alloying mechanisms between the Cu(111) and Cu(100) where Rh atom place exchange into the terraces is facile on Cu(100). CO TPD and RAIRS experiments were conducted to study the Rh active sites in the RhCu(100) alloys. CO TPD experiments revealed CO desorption at both low and high temperature hinting at the existence of dicarbonyls, which had not previously been observed on SAAs. RAIRS was used to demonstrate that the low temperature peak corresponded to the transition from dicarbonyls to monocarbonyls and the high temperature peak involved the desorption of the monocarbonyls, which was further confirmed by DFT. Together, these results help us to understand the active sites in RhCu(100) SAAs and the influence of the coordination environment on the binding to Rh sites. These results will further shed light on the structural characterization of high surface area SAA catalysts.

5:20pm **HC+AS+SS-WeA-10 Crossing the Great Divide Again: Psuedo-Molecular Beams at Atmospheric Pressure**, *E. High,* ***Christian Reece***, Harvard University

In order to reliably predict catalytic activity, we require accurate and robust kinetic models. Fundamental surface science studies on model catalysts are generally considered the "gold standard" for measuring in-depth kinetic and mechanistic information. However, there is often a perceived difficulty in transferring this knowledge from ultra-high vacuum surface science to applied reactor conditions i.e., at elevated temperature and pressure. This misunderstanding led to the development of terms such as pressure gap. In reality this so-called pressure gap is in fact a pressure continuum, with the caveat that the catalyst state (i.e., the structure and composition) must be kept consistent across the pressure regimes [1,2]. Herein we demonstrate a high-pressure analogue to classic molecular beam experiments utilising a home-built transient flow reactor in order to directly compare results measured at UHV and at atmospheric pressure. Using CO oxidation over polycrystalline Pd as a test reaction, we find that the transient behaviour observed at UHV [3] is recreated in the transient flow reactor. Further, the fundamentally derived kinetic model that is used to describe the molecular beam experiments also recreates the transient behaviour observed at atmospheric pressure when fed into a packed bed reactor simulation.

[1] Reece, C., Redekop, E.A., Karakalos, S., Friend, C.M. and Madix, R., 2018. Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients. Nature Catalysis, 1(11), pp.852-859.

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5:40pm **HC+AS+SS-WeA-11 Self-Propagating High Temperature Synthesis of Chevrel Phase Sulfides from Elemental Precursors***, **Tessa Gilmore**, M. Pawar, P. Gouma,* The Ohio State University

Self-propagating high temperature synthesis (SHS) is a spontaneous, irreversible, combustion process that requires close to no energy to produce complex materials at high temperature through self-sustained reactions. Little is known about the mechanistic nature of this versatile process, which limits its controllability and applicability. Chevrel Phase (CP) compounds (MxMo6S8-CPs) constitute a class of multifunctional, ceramic, designer materials targeted for catalysis, battery electrodes, quantum computing, and other applications. In this research, the successful and rapid processing of the sulfide Chevrel compound Cu4Mo6S8 via SHS is demonstrated, and a mechanism is provided. Thermochemical measurements identify an atypical behavior for this SHS process where the overall reaction temperature does not surpass that of the materials with the lowest melting point. This result is attributed to intercalation assisted massive phase transformation facilitated by the use of a MoS2 precursor. Further work to synthesize the Chevrel phase using other cations is continuing.

6:00pm **HC+AS+SS-WeA-12 Growth and Activity of Ni Catalysts Supported over Ti-doped Ceria from Single Crystal Thin Films to Nanocrystals***, J. Miao, T. Ara, **Jing Zhou**,* University of Wyoming

Ceria-supported nickel catalysts have been of great interest in many important applications such as dry reforming of methane (DRM).[1] They can exhibit promising catalytic behavior owing to the unique redox properties of ceria as well as strong metal-support interactions. To enhance the thermal stability of ceria as well as improve its redox properties as a catalytic support for practical applications in catalysis, metal dopants such as Ti can be introduced into ceria. Our previous studies have shown that well-ordered (111)-oriented $Ce_{1-x}Ti_xO_{2-\delta}$ thin films can be prepared by simultaneous introduction of Ce and Ti onto Ru(0001) at 700 K in an oxygen environment.[2] The incorporation of Ti in ceria causes the partial reduction of Ce from +4 to +3 state. The films are of high quality consisting of flat terraces with surface features of ceria lattices, oxygen vacancies, Ti dopants, as well as domain boundaries. The extent of the Ce reduction and the nature of the surface structure correlate with the amount of Ti dopants in ceria. Compared to pure CeO_2(111), addition of Ti dopant in $Ce_{1-x}Ti_xO_{2-\delta}$(111) can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as smaller particles upon heating.[3] To study as practical catalysts, powder materials of 5 wt.% Ni dispersed over a series of $Ce_{1-x}Ti_xO_{2-\delta}$ (x: 0-0.5) were prepared using sol-gel and impregnation methods and investigated for the DRM reaction with a fixed-bed flow reactor, monitored by on-line mass spectrometer and GC instruments. Incorporation of Ti into the ceria lattice forming $Ce_{1-x}Ti_xO_{2-\delta}$ was observed with Ti/Ce ratios less than 3/7 and NiO is formed over these supports. The formation of segregated titania domains was also detected in $Ce_{1-x}Ti_xO_{2-\delta}$ with higher Ti/Ce ratios ($Ce_{0.6}Ti_{0.4}O_{2-\delta}$ and $Ce_{0.5}Ti_{0.5}O_{2-\delta}$). Both NiO and $NiTiO_3$ can be formed in these Ti-rich ceria supports. Our results demonstrate that doping Ti can enhance the reducibility of ceria and tune the Ni-support interaction, which result in an enhanced coke resistance and catalytic performance of Ni in DRM. The research is sponsored by the Carbon Engineering Initiative from School of Energy Resources at the University of Wyoming.

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Nanoscale Science and Technology Division
Room 304 - Session NS2+AS+EM-WeA

Scanning Probe Metrology of 1D and 2D Materials

Moderators: Maryam Ebrahimi, lakehead University, Canada, **Aubrey Hanbicki**, Laboratory for Physical Sciences

4:20pm **NS2+AS+EM-WeA-7 New on-Surface Synthesis Techniques for Creating Precise 1D Graphene Nanoribbon Heterojunctions and Device-Tunable 2D Molecular Arrays***, **Michael Crommie**,* UC Berkeley Department of Physics*; G. Dong,* University of Chicago Department of Chemistry*; J. Lischner,* Imperial College London Department of Materials, UK*; A. Zettl, P. Jacobse, Z. Wang,* UC Berkeley Department of Physics*; J. Yin,* University of Chicago Department of Chemistry*; H. Tsai, F. Liou, A. Aikawa,* UC Berkeley Department of Physics **INVITED**

Bottom-up fabrication techniques for assembling molecular nanostructures at surfaces typically exploit various surface interactions that (along with random thermal processes) can be biased toward achieving desired structural results via the clever design of molecular precursors. Great progress has been made using this approach, but surface-grown molecular structures remain plagued by random, uncontrolled processes that make complex structural control difficult. Overcoming this problem is one of the grand challenges of this subfield. Here I will discuss two new approaches to molecular surface assembly that have allowed us to improve order in surface-based nanostructures. The first involves 1D materials and utilizes a solution-based polymerization scheme combined with a new surface deposition procedure. The second involves combining molecular surface assembly with 2D field-effect transistors (FETs). The first method is focused on graphene nanoribbons (GNRs), nanometer-wide strips of graphene. Fabricating complex heterostructure sequences in GNRs remains a difficult challenge because we can't sequence GNRs the way we sequence DNA. This makes it hard to fulfill the promise of GNR-based molecular electronics because of the difficulty of fabricating GNRs composed of well-ordered segments that each have controlled properties (e.g., bandgap, doping, magnetism, optical response). We have made progress toward overcoming this challenge by using a new protecting-group-aided-iterative-synthesis strategy. This allows us to create GNR oligomers with perfectly defined monomer sequences in solution that can be deposited onto surfaces for cyclodehydrogenation using a matrix-assisted deposition (MAD) procedure. This has enabled the synthesis of GNR heterojunctions that would not be possible via other techniques. The second technique I will discuss involves the use of an "active substrate" (a graphene FET) to induce *reversible* 2D molecular assembly through a combination of Coulomb and van der Waals interactions. The trick here is to use a molecule (in our case F_4TCNQ) whose LUMO level (E_L) lies in an energy range accessible to the Fermi level (E_F) of the 2D FET. Manipulating E_F relative to E_L via the device backgate allows charge in the device to reversibly flow between substrate states and the LUMO level of adsorbed molecules. This results in unexpected mechanical responsivity of the molecules, including tunable 2D array formation and a reversible quasi-1D phase transition that we have imaged using scanning tunneling microscopy.

5:00pm **NS2+AS+EM-WeA-9 Temperature-Mediated Adsorption and Assembly of Internally Fluorinated Chevron Graphene Nanoribbon Precursors on Au(111)***, **Jacob Teeter**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; M. Sarker,* University of Nebraska - Lincoln*; C. Tao, J. Huang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; A. Sinitskii,* University of Nebraska - Lincoln*; A. Li,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

The archetypical chevron-shape graphene nanoribbon (GNR) broke new ground in the on-surface synthesis of carbon-based nanomaterials with its development in 2010 by Cai *et al*[1]. Subsequent innovation predicated on this discovery introduced a wide variety of GNRs with differing shapes, edge types, heteroatomic substitutions, topological phases, and more. One drawback to studying GNRs arising from surface-assisted synthesis is the intrinsic electronic hybridization between the GNR and the surface upon which it was grown. This convolutes electronic characterization such as scanning tunneling spectroscopy (STS), but can be mitigated somewhat through tip-based manipulation of the GNRs onto an insulating layer on the surface, or by introducing a powder of solution-synthesized GNRs to a semiconducting substrate. Only recently has a method been developed - utilizing rutile TiO_2(011), rationally designed fluorinated precursors, and a surface-assisted cyclodehydrofluorination reaction - to achieve bottom-up-synthesized atomically precise GNRs on such a surface[2].

In this work, we have developed more fluorinated precursors to expand the set of atomically precise GNRs grown on semiconducting surfaces and studied their assembly on Au(111) using scanning tunneling microscopy. In particular, we have produced and prototyped on Au(111) a fluorinated chevron precursor intended to yield chevron-type GNRs on TiO_2(011). With all other factors equivalent, the adsorption of the precursor is heavily dependent on the temperature of the surface of the Au(111) crystal on which it is deposited. The lack of adsorption at room temperature is in sharp contrast with the non-fluorinated precursor, which can be deposited at room temperature and post-annealed to produce GNRs in good yield. We attribute this discrepancy to interactions between the internal F atoms and the Au(111) surface, which is supported by theoretical calculations.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

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5:20pm **NS2+AS+EM-WeA-10 STM Study of Superconducting Film FeTe(1-x)Se(x) on Topological Insulator Bi_2Te_3*, Hoyeon Jeon*,** *W. Ko, M. Brahlek, R. G. Moore II, A. Li,* Oak Ridge National Laboratory, USA

Topological superconductors (TSCs) have attracted great attention because they can host Majorana fermions for quantum computation. Because natural TSCs are rarely found, alternative ways to make TSCs are badly needed. One of them is using proximity effect by combining two-dimensional Dirac surface states of topological insulator (TI) with s-wave superconductivity (SC) to generate localized topological Majorana zero modes in vortex cores. Here we report the epitaxial growth of SC films of FeTe(1-x)Se(x) on TI of Bi_2Te_3, their electronic structures and surface inhomogeneities of superconductivity using scanning tunneling microscope/spectroscopy (STM/STS). A variety of samples are examined with different thicknesses of superconducting layer and selenium concentrations. We expect our results to be relevant for searching for materials platforms to host topological superconductivity.

The research is supported by the U.S. Department of Energy (DOE), Office of Science, National Quantum Information Science Research Centers., the Quantum Science Center (QSC), a National Quantum Information Science Research Center of the U.S. Department of Energy (DOE).

5:40pm **NS2+AS+EM-WeA-11 Atomic-Scale Mapping of Thermoelectric Properties of Noble Transition Metal Dichalcogenides*, Saban Hus,*** *A. Li,* Oak Ridge National Laboratory*; L. Liu, Y. Chen,* Purdue University

Monolayer noble transition metal dichalcogenides with hexagonal lattice structure are predicted to be high performance thermoelectric materials at room temperature [1]. Their pentagonal counterparts promise even better performance due to the in-plane anisotropy of the lattice [2]. However, like many other features of 2D materials, their thermoelectric properties can significantly be altered by the heterogeneities in the atomically thin layers [3]. Using a scanning tunneling microscope (STM), we investigate the thermoelectric properties of both pentagonal and hexagonal noble transition metal dichalcogenide monolayers in atomic resolution. We observe that atomic-scale defects and variations in 2D layer-substrate interface create a rich thermoelectric landscape invisible to mesoscopic scale measurements. Precise control and utilization of these heterogeneities can lead to next-generation thermoelectric devices and materials for energy applications.

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* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

Surface Science Division
Room 319 - Session SS+AS-WeA
Memorial Session in Honor of Patricia Thiel I

Moderators: Alex Belianinov, Oak Ridge National Laboratory, **Dapeng Jing**, Iowa State University

2:20pm **SS+AS-WeA-1 Assembly and Stability of Metal Nanoclusters at Surfaces: Modeling Inspired by Thiel-Group STM Studies*, Jim Evans,*** *Y. Han,* Iowa State University*; D. Liu,* Ames Laboratory USDOE*; K. Lai,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

STM studies by the Thiel group have characterized diverse non-equilibrium growth shapes for 2D metal nanoclusters (NCs) formed by deposition on strongly-binding metal surfaces, as well as the NC size and spatial distributions [1,2]. More recent work also considered deposition on a weakly-binding graphite substrate, producing not just supported 3D NCs, but also NCs intercalated beneath the top graphene layers [3]. These observations have guided development of predictive atomistic-level modeling of all aspects of the nucleation and growth process. For example, this modeling successfully captures the growth morphologies of individual NCs: fractals for limited periphery diffusion, height selected NCs due to quantum size effects; core-ring vs intermixed alloy structures for co-deposition; star-fish NCs on 5-fold quasicrystal surfaces; “squeezed” 3D NCs for intercalation, etc.

These arrays of supported metal NCs are metastable, and thus coarsen to fewer, larger NCs (reducing the energy cost of broken bonds at NC peripheries) on a time-scale typically significantly longer than that for deposition. In contrast to the expected Oswald Ripening (OR), the Thiel group showed for metal(100) homoepitaxy, coarsening was dominated by 2D NC diffusion and coalescence, i.e., Smoluchowski Ripening (SR) [4]. This observation has prompted extensive theory development for the NC size-dependence of diffusion (as this controls SR kinetics). For metal(111) homoepitaxy where OR occurs, the Thiel group explored the dramatic acceleration of OR due to even trace amounts of chalcogens due to the formation of metal-chalcogen complexes [4]. This work has also prompted extensive recent theoretical development.

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2:40pm **SS+AS-WeA-2 Stability and Dynamics of Sulfur-Metal Complexes on Coinage Metal Surfaces*, Da-Jiang Liu,*** Iowa State University **INVITED**

Interactions between sulfur and other chalcogen atoms and metal surfaces are critical in areas such as heterogeneous catalysis, self-assembled monolayers, and 2D materials. Over the last decade, Prof Thiel's research group has conducted a systematic survey of adsorption of sulfur on various high symmetry surfaces of Cu, Ag, and Au using low temperature STM. A rich variety of sulfur-metal surface complexes have been observed, depending on the type of metal, the coverage of sulfur, and the surface orientation.

Identification of those complexes is facilitated by density functional theory (DFT) studies, which provide information regarding energies, geometries, and simulated STM images. Those sulfur-metal complexes are crucial for mass transport that affects surface morphology. Molecular dynamics simulations using machine learning potentials trained from DFT calculations provide insights regarding the the role sulfur plays in

enhancement
of surface mass transport.

3:00pm **SS+AS-WeA-3 The Atomic of Structure of Surfaces: From Vacuum to Gas and Liquid Environments*, Miquel Salmeron,*** Lawrence Berkeley National Laboratory **INVITED**

The development of spectroscopies (XPS, XAS) and microscopies (STM) that can operate in ambient gas pressures has revealed that the structure of material surfaces depends strongly on the environmental conditions of gas composition, pressure and temperature. Experiments have shown that adsorption of atoms and molecules can substantial restructure surfaces that are otherwise stable under vacuum conditions. Restructuring is manifested in the breaking on the initially flat crystalline surface by formation of nanoclusters from atoms detached from steps and other defects. In the case of alloys, adsorbed species change the surface stoichiometry by inducing segregation of alloy components. This restructuring is important because the catalytic activity and selectivity of catalyst surfaces can be strongly modified.

I will discuss the possible generality of this phenomenon by analyzing cases where atomically flat surfaces of many transition metals undergo such changes in the presence of CO even at cryogenic temperatures, while others remain unchanged

4:20pm **SS+AS-WeA-7 The Influence of Alloying on Surface Kinetics*, Karina Morgenstern,*** Ruhr-Universität Bochum, Germany **INVITED**

The physical properties of nanoscale systems differ from those of macroscopic systems, making them attractive candidates to tune the electronic or optical properties of matter. However, nanostructures are thermodynamically only metastable, altering their shape and thus their properties even at room temperature [1]. Patricia Thiel and coworkers extended this work from vacuum to coarsening in the presence of chalcogens [2] and pioneered work for heteroepitaxial systems [3]. Following the latter, we use Ag/Cu(111) that serves, at a lattice mismatch of 13%, as a representative for a large deposit on a substrate with a small lattice constant. This large difference influences growth, induced growth, and decay of Ag nanoislands on Cu(111) as revealed by variable temperature scanning tunneling microscopy [3]. For natural growth, the dimensionality of the structures depends on temperature. A layer-by-layer growth at low temperature suggests that low-temperature growth might be an effective way to overcome the kinetic limitations of the step edge barrier for forming smoother interface layers. Similar, but not identical clusters can be induced from a 2D gas by scanning the surface at elevated voltages. The higher temperature islands exhibit a misfit dislocation pattern, which influences their decay. We relate specifically stable, magic island sizes to the complexity of the heteroepitaxial decay. Even more unusual is the decay of Cu-Ag core-shell islands, for which we discuss two qualitatively different types of decay mechanisms [5]. The implication of the kinetics. for the physicochemical properties of the nanoparticles are discussed in this talk.

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5:00pm **SS+AS-WeA-9 Cluster Superlattice Membranes*, Thomas Michely,*** University of Cologne, Germany **INVITED**

Cluster superlattice membranes are a new type of a 2D material consisting of a two dimensional (2D) hexagonal lattice of similar-sized nanoclusters sandwiched between a single-crystal 2D layer and an embedding matrix material. The fabrication process involves three main steps, the templated self-organization of a cluster superlattice on the moiré of a 2D layer with a metal substrate, conformal embedding in a matrix, and subsequent lift-off from the metal substrate. The mechanical stability provided by the matrix of nm-thickness makes the membrane stable as a free-standing material and enables transfer to other substrates. The fabrication procedure is proposed to be applicable to a wide variety of cluster materials and cluster sizes from the single-atom limit to clusters of a few hundred atoms, as well as to several 2D layer/host matrix combinations.

In this talk we will exemplify the cluster superlattice membrane concept for Ir clusters on graphene or a monolayer of hexagonal boron nitride and embedded in a carbon matrix. The membrane fabrication process is characterized step-by-step using scanning tunneling microscopy and spectroscopy, x-ray photoelectron spectroscopy, optical and transmission electron microscopy, as well as Raman spectroscopy.

The versatility of the membrane composition, its mechanical stability, and the simplicity of the transfer procedure make cluster superlattice membranes a promising material in catalysis and magnetism, for which potential applications are outlined.

The contributions of Pantelis Bampoulis, Tobias Hartl, Moritz Will, Stefan Schulte, Kai Kämper, Davor Čapeta, Rajendra Singh, Daniel Scheinecker, Virginia Boix de la Cruz, Sophia Dellmann, Paolo Lacovig, Silvano Lizzit, Boris V. Senkovskiy, Alexander Grüneis, Marko Kralj, Jan Knudsen, and Jani Kotakoski to this work are gratefully acknowledged.

5:40pm **SS+AS-WeA-11 High Quality 2-D Materials Characterized Paradoxically from Broad Diffraction Features.*, Michael Tringides,*** Iowa State University and Ames Laboratory US-DOE **INVITED**

Paradoxically a very broad diffraction background, named the Bell-Shaped-Component (BSC), has been established as a feature of graphene growth. Recent diffraction studies as a function of electron energy on Gr/SiC have shown that the BSC is not related to scattering interference. The broad background is in-phase with the Bragg component of both the (00) and Gr(10) spots. Instead textbook diffraction states it should be out-of-phase, since it should originate from destructive interference between adjacent terraces[1]. Additional experiments were carried out as a function of temperature over the range 1200° C-1300° C that single-layer-graphene (SLG) grows. Quantitative fitting of the profiles shows that the BSC follows the increase of the G(10) spot, proving directly that the BSC indicates high quality graphene[2]. The BSC has been also in graphene on metals including Gr/Ir(111)[3]. Recent experiments also show that the BSC is present in h-BN films grown on Ir(111)[3,4]. Its presence in such a wide range of 2-materials suggests its origin must be general and fundamental related to the unusual single layer uniformity common to these widely varying films. One possible explanation of the BSC relates to electron confinement within a single uniform layer which suggests that the BSC is an excellent measure of their uniformity. The confinement of the graphene electrons and the corresponding spread in their wavevector has been seen with ARPES[5]. The transfer of the large momentum spread to the diffracted electrons requires better theoretical understanding of the graphene electron-beam electron interaction.

On a personal note this was one of the last but very enjoyable scientific interactions I had with Pat. From the very beginning she was very enthusiastic and insightful about the problem. This was particularly important because the results were unintuitive and unexpected. This is a statement to her unusual combination of strengths: an extraordinary scientist with deep insights and a warm communicative friend.

In collaboration with P.A.Thiel (deceased), M. Horn von Hoegen , E. H. Conrad.

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2D Materials Technical Group
Room 303 - Session 2D+AS+NS+SS-ThM

2D Materials: Scanning Probe Microscopy and Spectroscopy

Moderators: Matthias Batzill, University of South Florida, **Yi-Ting Hsu**, University of Notre Dame

8:00am **2D+AS+NS+SS-ThM-1 Atomically Precise Graphene Nanoribbons for Quantum Electronics*, An-Ping Li,*** Oak Ridge National Laboratory **INVITED**

An-Ping Li, Chuanxu Ma, Marek Kolmer, Wonhee Ko, Kunlun Hong, Peter Bonnesen, Alex Puretzky, Jingsong Huang, Liangbo Liang, Bobby Sumpter

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Graphene nanoribbons (GNRs) possess high mobility and current-carrying capability, sizeable bandgap, long mean free path, localized spin and topological edges states [1]. These properties make them attractive candidates for quantum electronic applications. Atomically precise GNRs can be synthesized bottom-up using controlled on-surface chemical reactions from rationally designed molecular precursors [2]. The on-surface reactions of molecular precursors performed under ultra-high vacuum conditions can further be combined with scanning tunneling microscopy (STM) for in situ characterization of atomic, electronic, and magnetic properties. In this talk, I will discuss our recent progress in realizing novel quantum states in GNR heterostructures at atomic precision. First, a bottom-up approach is developed to couple graphene nanodot (GND) covalently at the edges of GNR to create quantum-well-like states for well-defined narrow-band light emission [3], which highlights a route to programmable and deterministic creation of quantum light emitters. Second, atomically precise GNRs are obtained by the on-surface synthesis approach on a model metal oxide, showing entangled magnetic states decoupled from the substrate [4]. These works illustrate that by using bottom-up synthesis—complemented by advanced microscopy and spectroscopy, as well as theory/simulation to enable atomistic level control—a rational approach to graphitic quantum electronic materials can be established with atomic precise.

The research was conducted at the Center for Nanophase Materials Sciences (CNMS), a US Department of Energy User Facility. The electronic characterization was funded by ONR grants N00014-20-1-2302 and N00014-16-1-3153.

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8:40am **2D+AS+NS+SS-ThM-3 Band Gaps of Single-Layer Transition-Metal-Dichalcogenides Determined by Scanning Tunneling Spectroscopy*, Randall Feenstra,*** *G. Frazier, J. Lou,* Carnegie Mellon University*; Y. Pan, S. Foelsch,* Paul Drude Institute, Germany*; Y. Lin, B. Jariwala, K. Zhang, J. Robinson,* Penn State University

Using scanning tunneling spectroscopy at a temperature of 5 K, the electronic states of single-layer MoS_2 and WSe_2, grown on epitaxial graphene, have been investigated. Data is acquired utilizing a high-dynamic-range method in which the sample-tip separation is varied as a function of the sample-tip voltage (separation is decreased linearly as the magnitude of the voltage is reduced). Resulting spectra, when normalized to constant sample-tip separation, display conductance values that range over 5 – 6 orders of magnitude above the noise level [1]. The resulting edges of the conduction and valence bands, as well as onsets of higher/lower lying bands, are clearly defined. A theory for fitting the spectra is developed in which the varying wave-vector of the electronic states is explicitly included, yielding significant improvement in the quality of the fits compared to prior work [2]. Band onset energies can be determined with an accuracy of ~20 meV [1]. However, certain features in the data remain poorly explained by the model, in particular, an apparent broadening or smearing of the band edges which is 5x larger than that given by any instrumental effect (kT broadening together with modulation voltage of the measurement). Tentatively, this additional broadening is attributed to tip-induced band bending. Results of fitting which includes this effect will be described.

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9:00am **2D+AS+NS+SS-ThM-4 Open-Source Controller for Scanning Probe Microscopy Applications***, M. Kangül, N. Asmari Saadabad, M. Penedo,* ***Georg Fantner,*** École Polytechnique Fédéral de Lausanne, Switzerland

Transferring the outcomes of academic research into patented industrial products converts the conceptual proof into accessible and sustainable technology. However, it is not always beneficial for researchers; as scientific studies often push the limits of instruments, requiring custom functionalities. In order to resolve these needs, several options are available, among which, hacking off-the-shelf products or rebuilding a simple copy of the existing technology are the most common ones. Either of these solutions slows down the research in a multidisciplinary field like Scanning Probing Microscopy (SPM). To not be limited by the disadvantages of the aforementioned solutions, we have developed an open-source SPM controller as a technology that eases innovation in not only our research but also in the whole SPM community.

In this regard, we have chosen a modular design strategy. A commercial FPGA (NI-7856R) with embedded real-time controller code sits at the core of the controller hardware. An FPGA adapter board for the flexibility of choosing different FPGAs, interconnect boards to perform digitally controlled (SPI) analog signal conditioning, such as filters and gain-offset stages, and a microscope adapter board to easily customize the input/output terminals of the controller for various SPM instruments are the other components of the modular hardware design. To run the controller, a custom software suite was developed in the graphical programming language LabVIEW (National Instruments). Similar to hardware, the software is also implemented in a highly modular fashion. The functions have been formulated into separate modules with minimum cross-dependency to reduce the complexity of coding for new developers.

The interest of our scientific and industrial collaborators in adapting and using our SPM controller in their instruments has motivated us to put an extra effort into building supporting documentation and creating an open-source platform. For the hardware, the documentation comprises design files, manufacturing guides, and assembly notes. For the software, documentation explaining the functionality of the real-time controller is provided, while the user interface side of the software is documented with user guides.

Here we report an open-source modular SPM controller provided with detailed documentation on both hardware and software levels. Modularity and documentation make it an easy-to-adapt instrument for various SPM applications. This platform has already been successfully adapted to control different SPMs such as contact mode AFM, AM-AFM, high-speed off-resonance tapping mode AFM, scanning ion conductance microscope, correlative AFM/SEM, and STM.

9:20am **2D+AS+NS+SS-ThM-5 Activation of Resistive Switching in TaOx on the Nanoscale*, Olha Popova,*** ORNL

In present work we have shown two an alternative pathways to induce resistive switching of prototypical TaOx –(1) via direct biasing with a nanoscale AFM probe in oxygen free environment and (2) via He-ion patterning. Both approaches were carried out with fine control over the net amount of dissipated energy during activation. With direct AFM probe activation in oxygen free environment, we were able to switch conducting properties of the material in poorly controlled conditions. This is a similar pathway to electroforming, albeit combined with microscopy, which revealed directly the changes induced in the film during field-induced insulator-metal transition. Filamentary regions down to 20 nm in dimension could be routinely achieved by reducing the peak current during the activation cycle. Nevertheless, the process remains extremely stochastic. In contrast, by use of He ion irradiation pristine insulating state can be easily converted to conducting and resistively switching state without any breakdown, but the transition itself is a smooth function of ion-irradiation dose. These findings revealed numerous intermediate states of TaOx can be created by controlled ion-irradiation. Remarkably, this effect is directly compatible with device architectures, potentially allowing for a high-degree of on-demand tunning of neuromorphic circuitry and materials. By combining AFM and SEM-CL we were able to determine dependence of the ion dose/materials damage correlated with the chemical, structural and compositional tunability of thin TaOx films which offers significant opportunities to neuromorphic nanoelectronic materials in comparison with more mature technologies based on traditional bulk electronic materials.

9:40am **2D+AS+NS+SS-ThM-6 Probing Sub-Nanoscale Photophysical and Photochemical Processes via Localized Surface Plasmons: Vibrational Nano-Spectroscopy*, Sayantan Mahapatra,*** *N. Jiang,* University of Illinois - Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offer about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of the surface adsorbed molecules with angstrom scale precision. In this work, we report a topological and chemical analysis of two regioisomers (positional isomers), trans- and cis-tetrakispentafluorophenylporphodilactone (trans- and cis-H_2F_{20}TPPDL) by scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has a wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics, etc. We have shown that it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, the nanoscale molecule-substrate interactions have been addressed at the single-molecule level by employing different single-crystals i.e., Ag(100), Cu(100), and Au(100). Strong surface interactions at Cu(100) surface converted the flexible porphodilactone structure inverted, which was further verified by STM. In another case, the chemical transformation of adsorbed ferrocene dicarboxylic acid molecule was also analyzed via TERS on Cu(100) due to significantly strong interaction. Apart from the Raman signal enhancement, the highly energetic localized surface plasmons generated at the tip apex were utilized for site-selective C—Si bond activation inside a single 5,10,15,20-(tetra-trimethylsilylethynyl)porphyrin molecule. The nano-confined plasmonic field dissociated only one chemical bond, in presence of multiple chemically equivalent bonds inside the single molecule. To this end, multiple sites were also activated one by one and different types of products were visualized which could prove extremely useful in plasmon-induced site-selective heterogeneous catalysis application.

11:00am **2D+AS+NS+SS-ThM-10 Visualize Emergent Electron Orders in Two-Dimensional Quantum Materials*, Xiaomeng Liu,*** Princeton University **INVITED**

Recent developments have enabled scientists to isolate various 2D materials and assemble them into van der Waals heterostructures with elaborate stacking and alignments. These van der Waals materials, constructed layer-by-layer, host numerous novel quantum phases. However, most studies so far are done by electrical transport measurements, lacking spatial and energy resolution. Scanning tunneling microscopes (STM) can provide unique insights to these emergent quantum phases by visualizing the electron wave function in real space. Using our recent study of the graphene quantum Hall system as an example, I will demonstrate using STM techniques to identify broken symmetries, visualize electron wavefunctions, and imaging quasiparticles.

11:40am **2D+AS+NS+SS-ThM-12 Reconstruct the Intrinsic Force Landscape of Interfacial Interaction with Excitation-Enhanced Force Spectroscopy*, Alan Liu,*** *T. Sulchek,* Georgia Institute of Technology

The advancement of sensitive force transducers has enabled scientists to measure the subtle forces of interactions between molecules and interfaces at nanometer scales. Force spectroscopy techniques, such as dynamic force spectroscopy (DFS), extract a single representative force from each measurement, and require thousands of measurements with model assumptions to extract useful physical parameters of the interaction. This process is not only time consuming, but also the preciseness of the results relies largely on model assumptions, which make the results highly variable and dependent on experimental conditions. Furthermore, because DFS models presume the interaction to be a reversible reaction under certain energy/force landscape, parameters extracted by DFS method can only represent the rough shape of interaction landscape but not able to probe the detail landscape of underlying intrinsic interactions. Using our recently developed force spectroscopy framework[1], we can obtain the definitive intrinsic force landscape using a high sampling rate (above 1 MHz) atomic force microscopy (AFM) measurement. While most studies deemed the "snap" of AFM force measurement as an instantaneous action, we successfully sampled the fluctuation and real-time movement of the AFM probe at snap under a high sampling rate. At the snap location of each AFM force-distance measurement, transition points can be identified that define the bound state (or probe-in-contact state) and unbound state (or free oscillation state). Sampling at these transition points are key to probe the normally inaccessible portion of force landscape where the intrinsic force landscape has higher force gradient than the stiffness of the force probe. Next, we demonstrated how to modulate the snap locations of the force-distance curves by tuning the bandwidth of the excitation applied to the AFM probe. Lastly, we integrated the definitive forces sampled at various locations to reconstruct the intrinsic force landscape of the interaction without any model assumption or curve fitting process.

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12:00pm **2D+AS+NS+SS-ThM-13 AVS Graduate Research Awardee Talk: True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy*, Saima Sumaiya*[1]**, *M. Baykara,* University of California, Merced

Atomic-scale characteristics of surfaces dictate not only the governing principles of numerous scientific phenomena ranging from catalysis to friction, but also the design and performance of billions of state-of-the art nanoscale devices ubiquitous in modern life. Despite such an enormous significance, our ability to visualize surfaces on the atomic scale is severely limited by the strict conditions under which the related methods are operated. In particular, the two prominent methods utilized to achieve atomic-resolution imaging – scanning tunneling microscopy (STM) and noncontact atomic force microscopy (NC-AFM) – are typically performed under ultrahigh vacuum (UHV) and often at low temperatures. Perhaps more importantly, results obtained under such well-controlled, clean environments bear little relevance for the great majority of processes and applications that often occur under ambient conditions. Therefore, a method which is able to reliably and robustly image surfaces with atomic-level spatial resolution under ambient conditions can be regarded as a "holy grail" of surface science. Here, we first show that the method of conductive atomic force microscopy (C-AFM) can be utilized to achieve true atomic-resolution imaging under ambient conditions by imaging single atomic vacancies on molybdenum disulfide (MoS_2), without any control over the operational environment or elaborate sample preparation. With our method, we are also able to image several other types of defects on MoS_2, demonstrating that C-AFM can be utilized to investigate surface defects in a reliable, straightforward fashion under ambient conditions, in contrast to the often extensive operational requirements of STM and NC-AFM. We further employ the method of C-AFM to record atomic-resolution images on different classes of materials such as gold (metal), WSe_2 (semiconductor), $PtSe_2$ (semimetal), and α-Mo_2C (metallic transition metal carbide), proving its versatility in terms of the material classes it can be applied to. Our approach overcomes many of the classical limitations associated with STM and NC-AFM, and the findings herald the emergence of C-AFM as a powerful tool for atomic-resolution imaging under ambient conditions.

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[1] **AVS Graduate Research Awardee**

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+AS+LS-ThM

Emerging Topics and Methods in Actinide/Rare Earth Science

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **Alison Pugmire**, LANL, **Paul Roussel**, AWE, UK

8:00am **AC+AS+LS-ThM-1 Nuclear Forensics 2020:A Strategic Inflection Point*, David Willingham,*** Lawrence Livermore Laboratory **INVITED**

The terrorist attacks of 9/11/01 greatly increased the visibility of nuclear forensics, as policy makers became increasingly concerned about the possibility of well-organized terrorist groups obtaining a nuclear weapon or dirty bomb.The Departments of Defense (DOD), Energy (DOE), Homeland Security (DHS), and State (DOS), as well as the Federal Bureau of Investigation (FBI) and the intelligence community, all play key roles in nuclear forensics. DHS, for example, was founded in November 2002 and included, from the start, a formal nuclear forensics program in its Science & Technology Branch.An August 2007 presidential decision directive established the specific roles these agencies would play and formally established the National Technical Nuclear Forensics Center (NTNFC) within DHS to coordinate planning, integration, assessment, and stewardship of the U.S. government's nuclear forensics capabilities. In 2010, the Nuclear Forensics & Attribution Act established a National Nuclear Forensics Expertise Development Program (NNFEDP) within the NTNFC aimed at “developing and maintaining a vibrant and enduring academic pathway from undergraduate to post-doctorate study in nuclear and geochemical science specialties directly relevant to technical nuclear forensics.”National laboratories like LLNL have particularly benefitted from the establishment of postdoctoral fellowships.

In 2021, primary responsibility for nuclear forensics within the US Government transferred from DHS to the National Nuclear Security Administration (NNSA) within DOE with the issuance of National Security Presidential Memorandum 35, National Technical Nuclear Forensics. However, the Nuclear Forensics & Attribution Act of 2007 is still in force, which defines certain roles for DHS, particularly for stewardship of the nuclear forensics’ workforce. Starting with the FY21 budget, there have been substantial increases in funding for NNSA for both nuclear forensic operations and R&D. However, the exact configuration of the nuclear forensics expertise development program(s) going forward is still being determined.”

This talk will highlight some of the outstanding research conducted by our DHS postdoctoral fellows, including:

1. Development of RIMS as a tool for in situ analyses for nuclear forensics.
2. Improved determination of half-lives and branching ratios important for U rad-chem
3. Exploration of the use of isochrons for age dating of impure samples.
4. Development of new stable isotopic systems as new sources of signatures for nuclear forensics.
5. Development of rapid methods for dissolving solid samples

8:40am **AC+AS+LS-ThM-3 The Non-Integer Occupancy Ground State Hypothesis*, Miles Beaux,*** Los Alamos National Laboratory **INVITED**

A deeply ingrained and long-standing practice exists for identifying integer orbital occupancy ground state electronic configurations for neutral atoms of the elements. For certain elements, the identification of the electron occupancies of the orbitals in a neutral atom can be a controversial topic, instigating heated debate among scientists. The pedagogy of how atomic structure and the periodic table are initially taught might serve as a driver for this practice. For example, the octet rule is often used to explain the most energetically favorable ionic states, similarities in properties of like-group elements, and the most stable compounds formed by the transfer and sharing of electrons. However, the octet rule is also insufficient to explain the existence, structure, and properties of transition metal elements, including the lanthanides and actinides.

A more fundamental quantum-based understanding of electronic structure provides a firm basis for the overall structure of the periodic table. Specifically, the octet rule is understood as the stability of completely filled *s*-, and *p*-orbitals each having electron capacities of two (l=0; m_l=0; $m_s=\pm\frac{1}{2}$) and six (l=1; m_l=-1,0,+1; $m_s=\pm\frac{1}{2}$), respectively, with each Period, *n*, having n_s and n_p orbitals (except for Period 1, for which no 1*p* orbital exists). Extrapolation of this quantum mechanical underpinning of the Periodic Table explains the existence of the *d*- and *f*-blocks. The filling patterns of the orbitals for elements in the Period Table reveals relative energies of the various orbitals. Deviations from the filling pattern are often explained to varying degrees of satisfaction by the interplay between Hund’s rule and the Aufbau principle for near-degenerate states; the stability of empty, half-filled, and completely filled orbitals; and core level screening. As the energy landscape for electron orbitals becomes more crowded for higher Period elements, the potential for near energy degenerate states increases. The potential for quantum superposition of electrons in these near energy states leading to effective non-integer orbital occupancies will be discussed in the context of observed instabilities in actinide and rare earth elements. Experimental and theoretical efforts to investigate this hypothesis for a series of Np, Pu, and Am compounds will also be described.

9:20am **AC+AS+LS-ThM-5 Legacy Plutonium at the Hanford Site*, Edgar Buck*,** *D. Reilly, G. Hall, K. Kruska, L. Liu, S. Triphathi, B. McNamara, A. Casella, D. Meier,* Pacific Northwest National Laboratory **INVITED**

The morphological characteristics of plutonium materials may provide information on the processes that were used to create the material; however, understanding of the detailed thermodynamic and kinetic processes needed to predict the evolution of its particle size distribution, crystal habit, and agglomerated state is still evolving. There has been an effort to fill this technical gap using an integrated experimental and modeling approach for formation of plutonium phases, including oxides and oxalates. Several different types of plutonium phases have been observed in wastes at the Hanford site, such as the Z9 crib near the former plutonium finishing plant and plutonium solids found in the SY102 and TX118 tanks. Laboratory experiments have been conducted to probe the formation mechanisms for these materials. By examining the preciptiating plutonium solids using a combination of in-situ optical microscopy (OM), scanning electron microscopy (SEM), cryo-electron microscopy (CryoEM) and in-situ transmission electron microscopy (TEM)., we have been able to demonstrate the occurrence of non-classical crystalline pathways for plutonium particle growth in some instances.

Understanding crystallization pathways in plutonium materials depends on the ability to unravel relationships between the intermediates and final crystalline products at the nanoscale, which is a particular challenge with radioactive materials. However, these powerful new tools of in-situ and cryoEM are providing new insights into the plutonium chemical system. The experimental data is helping to parameterize the computational modeling with the potential to lead to the development of predictive tools for identification.

11:00am **AC+AS+LS-ThM-10 Focused Ion Beam for Spatially Resolved Morphological Analysis of Nuclear Materials*, Brandon Chung*,** *S. Donald , D. Rosas, S. Sen-Britain, V. Som, N. Teslich, A. Baker,* Lawrence Livermore National Laboratory*; A. Ditter, D. Shuh,* Lawrence Berkeley National Laboratory

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. Conventional analysis using bulk nuclear material provides an overall analytical value, but a typical nuclear material is heterogeneous, requiring highly spatially resolved characterization. Consequently, averaging material characteristics may obscure critical forensic signatures resulting from local chemical and structural variations. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Our work shows the internal morphological and chemical variations in host nuclear materials provide valuable information about the material’s production processes and recent environmental exposures. We identified that internal microscopic features entrapped within bulk nuclear materials contain trace elements or chemical that are attributable to their origin, processing, and environmental exposures.

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Security Administration. This support does not constitute an express or implied endorsement on the part of the Government. LLNL-ABS-835643

11:20am **AC+AS+LS-ThM-11 Studying Combined Influence of Alpha Irradiation and Dissolved Hydrogen on UO_{-2} Corrosion Using a Microfluidic Electrochemical Cell*, Jennifer Yao*,** *B. McNamara, M. O'Hara,* Pacific Northwest National Laboratory*; N. Lahiri,* Pacific Northwest National Lab*; E. Ilton, C. Wang, E. Buck,* Pacific Northwest National Laboratory

It is well accepted concept that α-decay is the most important source of radiation in the spent nuclear fuel (SNF) after 1,000 years [1]. The influence of α-irradiation in the presence of dissolved H_2 on the corrosion of UO_2 can provide important information to assess the impact of the long-term SNF to the storage environment. However, experiments with bulk amount of SNF are expensive owing to the need for shielded hot cell facilities to protect researchers from the intense radiation field. To address this challenge, we employed a novel invention, particle-attached microfluidic electrochemical cell (PAMEC), to investigate UO_2 corrosion under different conditions (e.g., α-irradiation and H_2) at the microscale. Less than 10 µg of UO_2 (containing 1% to 10% $^{233}UO_2$) powder was mixed with polyvinylidene fluoride (PVDF) and carbon black to form the working electrode and included into PAMEC, which ^{233}U was used as alpha source to simulate the“aged” spent fuel [2]. The response of the corrosion potential of a ^{233}U contained UO_2 working electrode to dissolved H_2 in 0.1 M $NaClO_4$ (pH=9.5) will be presented. In addition, the 50nm thick Si_3N_4 detection window on PAMEC allows in situ imaging of the corrosion process using the high-resolution imaging technique, such as scanning electron microscope (SEM) coupled withEnergy-dispersive X-ray spectroscopy (EDS). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO_2 electrode that was exposed to alpha radiation and dissolved H_2. Our work demonstrates the study of combined influences on UO_2 corrosion under the conditions that are known to be present in the long-term SNF environment by employing a microfluidic electrochemical cell. We vision this approach can be widely applied to study the influences of conditions that resemble the practical repository environment on SNF, while with greatly reduced hazardous risk when performing such experiments.

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11:40am **AC+AS+LS-ThM-12 A Model to Extract the Size-Dependent Surface Structure of Actinide Oxide Nanoparticles*, Shinhyo Bang*,** *L. Moreau,* Washington State University

Characterization of actinide oxides at the nanoscale presents unique challenges due to their radioactivity, high surface area, and inherent diffraction broadening due to small grain size. Extended x-ray absorption spectroscopy (EXAFS) is an analytical method to investigate atomic-scale structural properties that enables their encapsulation and does not rely on long-range order. There is a limitation that EXAFS only gives the averaged structural information of heterogeneous samples. We aimed to deconvolute EXAFS results to extract the surface coordination environment of UO_2 NPs by proper modeling, and investigate how it evolves with varying sizes (1.4, 4.7, 8 nm). The termination effect was used to quantify the surface terminating species of UO_2 NPs. A higher degree of oxygenation on the surface was observed for 8 nm NPs. EXAFS simulation was implemented to backtrack the surface structure of these NPs. It was observed that the bond contraction due to the surface relaxation effect was localized in a few outermost layers of NPs and the surface disorder of 1.4 and 4.7 nm NPs was significantly enhanced from that of bulk.

Applied Surface Science Division
Room 320 - Session AS+AC+BI+CA+HI-ThM

Unraveling the Composition of Complex Systems with SIMS

Moderators: Steve Consiglio, Tokyo Electron, **Gregory L. Fisher**, Physical Electronics

8:20am **AS+AC+BI+CA+HI-ThM-2 Ex-Situ, Surface and Bulk Investigations of Defluxing Chemistry Effects on Solder Mask*, J. Elliott Fowler,*** Sandia National Laboratories*; R. Gerhardt,* Georgia Institute of Technology*; J. Ohlhausen, R. Callaway,* Sandia National Laboratories*; M. Watt,* Georgia Institute of Technology*; S. Grosso, S. Rosenberg,* Sandia National Laboratories

Solder masking is an integral process in the manufacture of printed circuit board assemblies (PCBAs) – it serves to protect the unfinished copper traces from environmental effects, define the soldering pads and provide an adherable surface for conformal coating. Liquid photo-imageable (LPI) solder mask is one of the most popular choices for PCBAs due to ideal electrical and physical properties as well as chemical. LPI solder mask is a heterogeneous epoxy acrylate-based matrix, thus its surface chemistry can be very distinct from its overall bulk chemistry. The surface chemistry is of particular interest as it must be compatible with and resistant to a wide range of chemistries and environments which the PCBA will experience during its production and fielding lifetime. For instance, sensitivity to moisture is a well-known issue. Several studies of solder mask moisture absorption reveal that it reaches a saturation of ~1 weight percent in high-humidity environments, and corresponding changes in insulative properties occur. Risks to mask performance have arisen as a result of the use of new flux formulations which require increasingly aggressive aqueous defluxing chemistries for removal. We hypothesize that alkaline defluxing chemistries will significantly modify the surface chemistry of solder mask, making it more vulnerable to moisture and thus deteriorating their insulative properties.

A commercially available LPI solder mask material was prepared on squares of FR4 board and exposed to increasingly alklaine cleaning chemistries: including DI water, a pH neutral and a pH >10 defluxing chemistry. Samples were tested with three complementary surface-sensitive analytical techniques, x-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS) and contact angle goniometry. TOF-SIMS results show that both pH neutral and alkaline chemistries alter the surface, removing PDMS and leaving organic residues. Contact angle goniometry shows that the alkaline chemistry makes the board’s surface significantly more hydrophilic. XPS results show a decrease in Si at the surface correlating to a decrease in PDMS versus the control, with the largest decrease occurring due to the alkaline chemistry. In all cases, the surface is somewhat recoverable; however, recovery is less pronounced with increasing pH. AC impedance spectroscopy and DC Surface Insulation Resistance (SIR) testing of exposed samples in elevated humidity environments was performed to resolve changes in insulative performance due to observed changes in mask surface chemistry.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

8:40am **AS+AC+BI+CA+HI-ThM-3 Unraveling the Composition of Complex Systems with SIMS*, Birgit Hagenhoff,*** Tascon GmbH, Germany **INVITED**

For more than four decades SIMS has proven to be a valuable tool in academic research as well as for industrial applications. Whereas the first years focussed on understanding the underlying physical processes using mono-elemental samples, the advent of ToF-SIMS (Time-of-Fligt Secondary Ion Mass Spectrometry) instrumentation in the 80s of the last century opened the path to using SIMS as a screening tool for characterising “the unknown”, i.e. samples about which hardly anything is known before the analysis, where sample preparation should be as scarce as possible and where the analysis is performed without any chromatographic pre-step to separate out sample compounds.

Over the years, intensive discussions between those developing instruments and those applying them on a daily basis lead to a fruitful and steep learning curve in the SIMS communities. Meanwhile SIMS instruments offer a multitude of operational modes and are capable of analysing as 3D volume pixel by pixel. The lateral resolution has almost reached the physical limit of the collision cascade with values well below 100 nm and a depth resolution in the nm-range can be achieved. The development of cluster ion sources leads to the possibility to also probe organic materials in depth. At the same time data evaluation routines have become more powerful to address the large amount of data (several GByte for a 3D data set).

Generally, users would like to address three main questions: what (identification) is sitting where (localization) and how much is it (quantification)? Whereas the localization problem, as mentioned above, meanwhile is comparatively straightforward, identification and quantification still are challenging. In identification, the parallel presence of many elements and organic compounds in the SIMS spectra still asks for an expert to solve the analytical puzzle. Here, the application of multivariate statistical techniques and, more recently, machine learning approaching offer promising paths into the future. For a reliable quantification, the influence of the SIMS matrix effect on the results has to be taken into account. Here, the availability of suited reference samples plays a key role for closing the gap to quantitative techniques, like e.g. XPS (X-ray Photoelectron Spectroscopy).

The talk will therefore focus on identification and quantification issues including the use of multivariate statistics, MS/MS approaches and the use of reference sample comparing SIMS with the quantitative techniques XPS and LEIS (Low Energy Ion Scattering).

9:20am **AS+AC+BI+CA+HI-ThM-5 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) as a Novel Approach to the Characterization of Coatings and Interfaces of Porous Transport Layers***, **Genevieve Stelmacovich**, M. Walker, J. Foster,* Colorado School of Mines*; D. Cullen ,* Oak Ridge National Laboratory*; A. Paxson ,* Plug Power*; G. Bender, T. Schuler, S. Ware,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

The United States energy infrastructure aims to move towards the integration of hydrogen energy. As such, the production of reliable hydrogen generation through the optimization of water electrolyzers is imperative. In proton exchange membrane water electrolyzes (PEMWE's), the porous transport layer (PTL) plays an important role. Due to the harsh conditions of the cell, titanium is the current state-of-the-art anode PTL material. However, titanium quickly forms a layer of titanium oxide which significantly decreases conductivity of the PTL and respectively decreases the overall efficiency of the PEMWE system. To mitigate oxide effects, coatings are commonly applied to the PTL.

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) in conjunction with Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) analysis is a commonly used technique to characterize PTL materials and PTL coatings, specifically to look at coating homogeneity and unfavorable oxide layer formation. Unfortunately, this approach is both time-consuming and labor intensive. Additionally, STEM-EDS analysis only provides elemental information, so if several oxide layers preside, it can be difficult to differentiate them, and thus lead to a lack of understanding fundamental degradation mechanisms. These technique deficiencies have motivated the development of an alternative approach that allow more efficient characterization of these materials. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a valuable technique that is commonly used to characterize thin films and buried interfaces. ToF-SIMS can be performed relatively quickly, provides chemical information, and is sensitive to trace elements. This technique also enables visualization of elemental distribution, which provides more detailed surface and interface information. This presentation will demonstrate capabilities of ToF-SIMS for characterization of PTLs comparing results to TEM analysis of cross-sections obtained with FIB-SEM. This study will highlight similarities and differences between the techniques, expand on technique optimization for these morphologically challenging samples, and suggest paths for future investigation moving forward.

9:40am **AS+AC+BI+CA+HI-ThM-6 Construction of Accurate 3D NanoSIMS Depth Profiling Images of Cells in the Presence of Lateral Variations in Sputter Rate***, M. Brunet, B. Gorman, **Mary Kraft**,* University of Illinois Urbana-Champaign

We have developed a strategy for constructing accurate 3D NanoSIMSdepth profiling images of cells in the presence of lateral variations in sputter rate. In this strategy, we use the secondary electrons acquired in parallel with the negative ions during depth profiling to reconstruct the 3D morphology of the cell every time a depth profiling image is acquired. The morphologies created for each raster plane in the depth profile are adjusted to ensure that the height at every pixel decreases with increasing image plane. The resulting reconstructions of the cell's morphology are used to define the z-positions of the voxels in the component-specific 3D NanoSIMS images. We validated this strategy by comparing morphology reconstructions for secondary electron depth profiling images acquired with focused ion beam - secondary electron microscopyand AFMdata acquired from the cell before depth profiling. The shape, curvature, and relative height of the reconstructed morphology agreed well with the AFM data. Depth correction of 3D NanoSIMSdepth profiling data of a metabolically labeled mammalian cell using this strategy improved visualization of the^{18}O-cholesterol and ^{15}N-sphingolipids distributions intransport vesicles and organelle membranes. Accurate 3D NanoSIMS images that show the intracellular distributions of molecules of interest may now be constructed in the presence of variations in sputter rate and the absence of correlated topography data.

11:00am **AS+AC+BI+CA+HI-ThM-10 Innovations in Nuclear Materials Analysis with SIMS***, **Christopher Szakal**,* National Institute of Standards and Technology (NIST) **INVITED**

Global nuclear safeguards efforts, coordinated by the International Atomic Energy Agency (IAEA), require precision measurements to answer questions related to nuclear treaty compliance. Despite those questions seeming relatively simple, and the elemental composition of the target analytes often consisting of just uranium and oxygen, the complex processes employed to answer those questions reveal the importance of subtle nuances to meet analytical objectives. This presentation will explore the complexity of this type of analyte system and how innovations in secondary ion mass spectrometry (SIMS) resulted in a routinely utilized tool to address nuclear safeguards requirements for environmental sampling analysis. The complexity is largely driven by the small amounts of nuclear particle material available for analysis, including challenges for 1) representative sampling of analyte material to represent actual nuclear processes, 2) accuracy and precision of uranium isotopic analyses across a wide dynamic range, and 3) determining when a nuclear process created the analyte material. Precision SIMS measurements provide the opportunity to address these analytical complexities to answer key nuclear safeguards questions, but the presentation will also highlight when limitations are inevitable for which questions can be answered.

11:40am **AS+AC+BI+CA+HI-ThM-12 Understanding Surface Bonding and Molecular Structure with MS/MS Imaging: From Click-Chemistry to Biogenesis***, **Gregory L. Fisher**,* Physical Electronics

A TOF-TOF imaging mass spectrometer allows TOF-SIMS (MS^1) imaging and tandem MS (MS^2) imaging to be achieved in a lossless fashion [1,2]. Secondary ions for MS^1 and MS^2 analysis are produced from the same surface area by a primary ion nanoprobe. Monolayer film samples may be characterized without undesired erosion or degradation; even sub-monolayer 2D films are readily characterized. Kilo-electron volt collision-induced dissociation (keV-CID) enables compositional identification and structural elucidation of precursor ion moieties. This analytical capability has been brought to bear for straightforward molecular identification as well as multifaceted studies involving surface modification, polymers, composites, catalysis, forensic and failure analysis, biology and pharmaceuticals. TOF-SIMS tandem MS imaging was employed to unravel the click-chemistry of sub-monolayer films [3] and shed new light to unlock the mystery of molecular biogenesis [4,5].

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12:00pm **AS+AC+BI+CA+HI-ThM-13 Probing Grain Boundary Segregation in 304L Stainless Steel using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)***, **James Ohlhausen**, E. Barrick, D. Susan, C. Robino, K. Hattar, J. Herrmann, P. Duran, J. Rodelas,* Sandia National Laboratories

Boron-rich phases in austenitic stainless steels can promote liquation cracking in the heat affected zone during welding. Stainless steels with boron concentrations even as low as 20 wt. ppm are susceptible to grain boundary cracking after heat treatments. The kinetics of phase transformations during heat treatment that generate the crack susceptible microstructure are currently unknown. Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to map Boron at grain boundaries and in the bulk at trace levels for a series of 304L stainless steel coupons that were heat treated across a range of temperatures and cooling rates to investigate these phase transformations.ToF-SIMS and Scanning electron microscopy (SEM) were used to observe the distribution of chromium borides before and after heat treatment. These results will be used to enable quantitative prediction of thermal processing conditions to avoid weld cracking.Sample preparation methods, ToF-SIMS acquisition conditions and data analysis will be discussed.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

Electronic Materials and Photonics Division
Room 304 - Session EM+AS-ThM

Photovoltaic Materials, Characterization, and Applications

Moderator: Seth King, University of Wisconsin - La Crosse

11:00am **EM+AS-ThM-10 Translating Materials-Level Characterization of Carbon-Nanotube-Reinforced Composite Gridlines To Module-Level Degradation***, **Sang Han,*** The Univeristy of New Mexico and Osazda Energy*; A. Chavez,* The University of New Mexico and Osazda Energy*; B. Rummel,* The University of New Mexico and Osazda Energy*; A. Jeffries,* Osazda Energy*; N. Bosco,* National Renewable Energy Laboratory*; B. Rounsaville , A. Rohatgi,* Georgia Institute of Technology

Cell cracks in PV modules caused by environmental stressors and extreme weather events can lead to gradual or immediate power degradation. To directly address cell-crack-induced degradation, we have formulated a carbon nanotube additive for commercial silver pastes used in screen printing. We have shown in earlier work that these metal matrix composites do not impact the cell efficiency, while enhancing the metallization's fracture toughness and electrical gap-bridging capability. In this work, we focus on translating materials-level characterization techniques to module-level degradation. We found that we get conflicting results from two different materials characterization methods of measuring the metallization's ability to electrically bridge gaps in cracked solar cells. To determine which materials characterization method correlates better with the mini-module degradation characteristics, we have conducted stress testing for a small dataset of mini-modules.

The first characterization method for measuring the metallization's ability to electrically bridge cell cracks is dubbed as Resistance Across Cleaves and cracKs (RACK), in which a piezoelectric stage pulls apart fractured cells in submicron increments while the resistance of the gridlines on top of the fractured cells is measured until the gridlines electrically fail. The tensile stress applied to the metallization during the RACK test is intended to mimic the stress encountered by the metal gridlines during thermal cycling after cell fracture, in which cell fragments translocate within the module. Another common method for characterizing the metallization's ability to electrically bridge cell cracks is three-point bending test, where a rectangular substrate with two parallel gridlines, laser-diced from a cell, is mounted on an acrylic beam and placed in a three-point bend fixture while the resistance of gridlines is monitored as a crack in the cell is slowly opened. The failure mechanism with this testing method could be an alternative representation of how a cell would fracture when the module is being flexed under heavy mechanical loads or being stepped on.

The two materials-level characterization methods described above are designed to measure the metallization's ability to electrically bridge a cracked cell; however, they give conflicting results as to which composition and geometry of carbon nanotubes performs best. To better understand which materials-level test correlates to module-level degradation, 2x2 minimodules were constructed with pre-fractured cells and subjected to thermal cycling.

11:20am **EM+AS-ThM-11 Effects of Carbon-Nanotube-Reinforced Composite Gridlines on Photovoltaic PERC Cell and Module Efficiency***, **Andre Chavez,*** The University of New Mexico and Osazda Energy*; S. Han,* The Univeristy of New Mexico and Osada Energy*; A. Jeffries,* Osazda Energy*; S. Huneycutt,* The Univeristy of North Carolina at Charlotte*; A. Ebong,* The University of North Caronlina at Charlotte*; D. Harwood, N. Azpiroz,* D2 Solar

Abstract — The addition of carbon nanotubes (CNTs) in commercial silver pastes used for the front metallization of Passivated Emitter and Rear Contact (PERC) solar cells not only helps improve the materials toughness and resilience to cell cracks, but also offers some improvement to cell efficiency. A large data set of 87 cells containing the CNT-enhanced metal matrix composite (MMC) gridlines, when compared to a set of 66 baseline PERC cells, shows an increased efficiency by 0.03%, which is the threshold that cell and module manufactures care about. Six mini-modules, each of which consists of two PERC cells connected in series, were fabricated with the baseline metallization, and six mini-modules were fabricated with MMC-enhanced PERC cells. Three modules were subjected to 200 cycles of thermal shock (TS) from -40 to +85 °C, and the remaining three were subjected to highly accelerated stress testing (HAST), where damp heat is applied at 120 °C for 100 hours and 100% relative humidity. After these two tests, the MMC metallization shows comparable corrosion to the baseline metallization and power loss of less than 0.6% after TS-200 and less than 4% after HAST-100. The inclusion of CNTs to conventional screen printable silver pastes has the ability to improve cell efficiency, while showing statistically identical beginning-of-life cell and module performance as well as corrosion characteristics and infant failure rate (e.g., solder bond failure) comparable to the baseline. These results show strong promise for commercial implementation of the MMC-enhanced metallization to improve PV module reliability.

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office Award Number DE-EE0009013.

11:40am **EM+AS-ThM-12 Atomic Layer Deposition of NiO for Single Junction Perovskite and Tandem Perovskite/Silicon Photovoltaics***, N. Phung, C. van Helvoirt,* Eindhoven University of Technology, The Netherlands*; D. Zhang, V. Zardetto, B. Geerligs,* TNO Science and Industry, the Netherlands*; M. Verheijen, E. Kessels, B. Macco, **Mariadriana Creatore,*** Eindhoven University of Technology, The Netherlands

Metal halide perovskite absorbers have attracted major attention due to their excellent opto-electronic properties. Recent advancements in performance and stability of perovskite solar cells (PSCs) have been achieved with the application of self-assembled monolayers (SAMs), serving as hole transport layers in the p-i-n PSC architecture [1]. However, a reproducible implementation of SAM in the PSC device requires knowledge of its surface coverage on ITO since non-covered areas in direct contact with perovskite may lead to shunts and low open-circuit voltage.

In this contribution, we investigate the influence of an atomic layer deposited (ALD) NiO film (7 nm) on the surface coverage of SAM for single junction PSC as well as tandem PSC/silicon devices. NiO is processed either by plasma-assisted ALD [2] or thermal ALD [3]. The latter has also been developed since thermal ALD is often adopted in upscalable technologies such as batch and spatial ALD.

We observe that the SAM of MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid) inhomogeneously covers ITO. Instead, when adopting NiO as intermediate layer between ITO and SAM, the SAM homogeneity and surface coverage improve, as witnessed by transmission electron microscopy (TEM) and conductive atomic force microscopy. This result is explained in terms of chemisorption reactions between SAM phosphonic acid groups and NiO hydroxyl groups. The SAM homogeneity on NiO leads to higher shunt resistance in the device with respect to the one with SAM directly processed on ITO. Moreover, the combination of NiO and SAM results in a narrower distribution of device performance reaching more than 20% efficient champion device.

The above-mentioned merits of ALD NiO are further exploited in a monolithic tandem device, consisting of a c-Si passivated emitter rear cell (PERC) bottom cell and a perovskite top cell. In the case of ITO/SAM tunnel junction, several devices present electrical shunts in the top cell, leading to a standard deviation of efficiency of 4.6% across device batches. In the case of ITO/NiO/SAM tunnel junction, the tandem device exhibits a narrow distribution of efficiency (standard deviation of 2% across device batches) because of the uniformity and conformality of NiO on ITO, as witnessed by TEM analysis. A champion efficiency of 23.7% is recorded, among the best tandem cell efficiency implementing an industrial standard bottom cell.

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[4] Phung, *et al.* (2021) ACS Appl. Mat. Interfaces, 14(1), 2166.

12:00pm **EM+AS-ThM-13 XPS Depth Profiling of Single Film and Two-Layer Heterojunction Metal-Halide Perovskites***, **Jennifer Mann,*** Physical Electronics*; C. Clark, W. Hsu, E. Pettit,* University of Minnesota*; K. Artyushkova,* Physical Electronics*; R. Holmes,* University of Minnesota

The goal of an XPS depth profile is to obtain accurate identification of layer thicknesses and 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.

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.

Organo-metal-halide perovskites are of interest due to their promising application in solar cells, where they have achieved efficiencies above 25%.In this work, we present XPS depth profiles of single films of metal-halide perovskites, with an ABX_3 structure(A = MA - methylammonium or Cs, B = Sn or Pb, X = Br or I).Maintaining stoichiometry while sputtering can be very challenging, so in addition, $MAPbI_3$ was analyzed with hard X-ray photoelectron spectroscopy (HAXPES). A Cr Kα (5414.8 eV) X-ray source provides information depths three times greater than the standard Al Kα (1486.6 eV) X-ray source.Using a higher energy photon provides a non-destructive method to probe deeper into the sample, minimizing the contribution from surface oxides and carbon contamination.

XPS depth profiles were obtained on a single layer perovskite film using the two cluster ion guns, available on the PHI *VersaProbe* III - C_{60} and argon gas cluster (GCIB) The viability of each gun in maintaining both the stoichiometry and chemistry of the film as it was sputtered was determined before measuring a more complex perovskite system.

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 the 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.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-ThM

Bridging Gaps III: Combined Theory and Experiment in Catalysis

Moderators: Liney Arnadottir, Oregon State University, **Sharani Roy**, University of Tennessee Knoxville

8:00am **HC+AS+SS-ThM-1 Mechanistic Understanding and Catalyst Design for Selective Methane Activations*, Ping Liu,*** Brookhaven National Laboratory **INVITED**

The development of variable catalysts to promote the activation of methane and control the conversion selectivity has long been a challenge in catalysis. One of the obstacles is the lacking in fundamental understanding of reaction network due to the complexity. Here, the mechanistic study of methane activation to carbon monoxide and/or methanol on metal/oxide and oxide/oxide will be presented using combined Density Functional Theory and kinetic Monte Carlo simulation. Our results not only provide new insight into the mechanism and active sites, but also highlight the importance of confined active site in tuning the binding of intermediates and promoting the catalytic performance.

8:40am **HC+AS+SS-ThM-3 A First Principles Study of Propane Dehydrogenation Reactions on Hydroxyl-Terminated Al_2O_3 Decorated Platinum Surfaces*, Sumandeep Kaur,*** *H. Nguyen, L. Árnadóttir,* Oregon State University

Propylene is precursor of many complex chemicals such as polypropylene, propylene oxide, acrylonitrile etc. which are used in the fabrication of numerous consumer and industrial products. Catalytic dehydrogenation of propane has been proposed as a practical route for propylene production and metal catalysts such as Pt, Pd and Sn have been extensively employed for this purpose. Recent experimental studies have shown that tailoring metal-active sites with atomic layer deposition (ALD) can increase the selectivity of propane dehydrogenation (PDH) towards propylene.[1] Herein we use DFT and microkinetic modeling to study PDH on Pt surfaces covered with Al_2O_3 to investigate the effect of ALD on PDH. Our primary results show that alumina ALD covers 1/6 of the planar surface Pt(111) blocking all the active sites for propane dehydrogenation while on the step or kink surfaces, (Pt(211), Pt(321), Pt(533)) alumina ALD forms a one-dimensional ribbon like structure along the step or kink atoms, leaning over the lower terrace and leaves room on the upper terrace for the reaction intermediates to interact with the ALD layer and the metal catalyst. These studies on PDH reactions on ALD covered Pt can lead to better understanding on how ALD can be used to tailor catalytic active sites and improve selectivity.

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9:00am **HC+AS+SS-ThM-4 Atomic-Level Studies of C_2H_4 on clean and Rh_1-Decorated $Fe_3O_4(001)$*, Panukorn Sombut,*** *L. Puntscher, C. Wang, M. Ulreich,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; J. Pavelec, Z. Jakub, F. Kraushofer, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; G. Parkinson,* TU Wien, Austria

The local binding environment of metal-oxide supported single-atom catalysts (SACs) determines how reactants adsorb and therefore plays a decisive role in catalysis. Here, we study how $Fe_3O_4(001)$-supported Rh_1 adatoms interact with ethylene (C_2H_4) using density functional theory, combined with temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. C_2H_4 is the simplest alkene molecule, and thus a model reactant for hydrogenation and hydroformylation reactions. Our study begins with the clean $Fe_3O_4(001)$ surface[1], where C_2H_4 binds weakly. We identify and model different molecule orderings at different coverages that agree nicely with STM images, as well as explain the experimental TPD data. Then, we study C_2H_4 adsorption at 2- and 5-fold coordinated Rh sites at the $Fe_3O_4(001)$ surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two C_2H_4 molecules, while 5-fold Rh can only host a single C_2H_4 molecule. Finally, we investigate coadsorption of C_2H_4 with CO, a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

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9:20am **HC+AS+SS-ThM-5 How the Support Dictates the Reactivity of FeO_x-Based Single-Atom Catalysts*, Matthias Meier,*** TU Wien, Austria **INVITED**

Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system[1], magnetite (Fe_3O_4), specifically its (001) facet has been used because it offers stable sites for single-atom adsorption up to high temperatures[2]. Here, I will demonstrate how important the support is for the stability of single-atoms, as well as their catalytic properties.

Rh and Ir single-atoms utilize Fe vacancies in the subsurface of the reconstructed $Fe_3O_4(001)$ unit cell to incorporate into the surface layer. Changing the positions of Fe atoms in the support as part of the incorporation process enables the single-atoms to be accommodated in a more favorable configuration than if they were adsorbing on top of the surface. Their catalytic properties are drastically affected by changes in the atomic environment. Incorporation temperatures vary depending on both coverage and the presence or absence of adsorbates, such as CO.

Changes in the support can affect not only ground states, but also reaction mechanisms and activation barriers. Pt single-atoms become mobile upon CO adsorption, forming dimers, which oxidize CO via a Mars van Krevelen reaction using a surface oxygen atom[3]. The support is temporarily altered, reducing overall activation barriers and permitting CO oxidation otherwise inaccessible at the observed experimental temperatures.

Similarly, subsurface vacancies are also present in $Fe_3O_4(111)$, modifying electronic surface states and allowing again for easy incorporation of single-atoms already at low temperatures, in line with experimental observations.

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11:00am **HC+AS+SS-ThM-10 Modifying Ethane Oxidation Selectivity on the stoichiometric IrO_2(110) surface through anion substitution*, Aravind Asthagiri,*** The Ohio State University **INVITED**

Selective alkane conversion to high value fuels or chemicals, such as methanol or ethylene, has drawn increasing interest due to abundance of natural gas. Recently, we reported a combined temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) study of below room temperature (T ~ 120 K) activation of methane on the stoichiometric IrO_2(110) surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on IrO_2(110) by creating some proportion of hydrogenated bridging oxygen (O_{br}-H) sites, which limit the oxidative capacity of the surface. This past work suggests that substitution of O_{br} sites with inert species may be an avenue to control selectivity between full and partial oxidation. We have used DFT to explore the effects of Cl substitution of O_{br}. Chlorine is isoelectronic to O_{br}-H and selective Cl substitution of O_{br} has been demonstrated on RuO_2(110) by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped IrO_2(110). We find that the Cl-doped IrO_2(110) is still facile in converting ethane to ethylene. In contrast, the ethylene selectivity step shows a strong effect due to Cl doping. Specifically, we find that H atom transfer from ethylene to the saturated O_{br} sites is unfavorable and therefore Cl doping will promote ethylene desorption over further reaction. DFT derived microkinetic simulations show that the selectivity of ethylene peaks at ~60% Cl substitution with increasing Cl substitution reducing the reactivity of ethane. Extending this work to other halogen anion substitutions (F, Br, I) shows that Cl is the optimal dopant. While Br and I favor ethylene desorption over further reaction, these dopants decrease ethane reactivity. In contrast, F dopant does not promote ethylene desorption versus reactivity as effectively as Cl. Current efforts to develop a microkinetic model to explore ethylene selectivity under reaction conditions will be discussed.

11:40am **HC+AS+SS-ThM-12 HC Graduate Student Finalist Talk: Insight into Subsurface Adsorption and Reconstruction of Ag(111) Deduced from a Lattice-Gas Model and Monte Carlo Simulations*, Carson Mize,*** University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; E. Lander, S. Roy,* University of Tennessee Knoxville

Gas-phase surface models are a beneficial, theoretical tool for providing qualitative insight into elementary steps of surface chemistry. Elementary steps, like adsorption, play a crucial role in many chemical phenomena like surface reconstruction and industrial heterogeneous catalysis. While there exist many previously developed gas-phase adsorption models, most models are limited to low adsorbate coverages due to the computational cost required to produce high coverage models. To investigate adsorption over a broad range of adsorbate coverages on a crystalline solid, we have developed a lattice-gas adsorption model that includes surface and subsurface adsorption, tunable interaction parameters calculated with density functional theory, and larger scale modeling with Monte Carlo simulations. This model has been applied to study oxygen adsorption on a Ag(111) surface, due to experimental findings suggesting the possibility of subsurface-adsorbed oxygen species. Our first model iteration included only strongest binding sites for each region and our simulations indicated greater oxygen accumulation in the second subsurface than the first subsurface in total coverages in excess of 0.375 monolayer (ML). Our second model iteration included all high symmetry sites in each region and found the same qualitative results as the first model using canonical Monte Carlo distributions. Additionally, current grand canonical distributions suggest some subsurface oxygen adsorption exists under temperatures of 475 – 550 K and pressures of 1 – 2 bar, which are typical industrial conditions for catalysis with these systems. Our current model includes adding Ag – Ag and Ag – O interactions to model surface reconstruction, as our previous models only included the unreconstructed silver lattice. This iteration will allow us to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4 × 4) and c(4 × 8) lattices, as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

12:00pm **HC+AS+SS-ThM-13 Measuring and Predicting a Key Catalyst-Performance Descriptor for Supported Metal Nanoparticle Catalysts: Metal Chemical Potential*, Charles T. Campbell,*** *J. Rumptz, K. Zhao,* University of Washington

Metal nanoparticles supported on high-area oxides and carbons form the basis for many catalysts and electrocatalysts. Their activity and stability depend on both particle size and choice of support. The chemical potential of the metal atoms in the catalyst material quantifies their stability and is a convenient descriptor that captures the effects of both the nanoparticle size and the support material on both surface reactivity and sinter resistance.[1,2] This chemical potential enters quantitatively into the rate equations for sintering, making a negative contribution to the activation energy.[2] Numerous experimental and theoretical studies have also found that the stability of metal atoms in catalyst materials, including alloys, correlates with their binding energies to adsorbates, whereby surface metal atoms that are more weakly bound to the solid interact more strongly with small adsorbates like O, CO, -OH and $–CH_3$.[1-3] It is thus desirable to develop methods to predict how metal chemical potential depends on particle size and support. Herein, we report calorimetric measurements of: (1) metal chemical potential as a function of particle size and support, and (2) the adhesion energy of the solid metals to different oxide and carbon supports.From these, we have identified predictive correlations of: (1) metal chemical potential in supported nanoparticles as a function of the particle size and the adhesion energy of the particle to the support, and (2) the dependence of this adhesion energy upon the metal element in the catalyst for oxide supports.

Work supported by DOE-OBES Chemical Sciences Division.

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Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room 301 - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Armin Golzhauser, Bielefeld University, Germany, **Shida Tan**, Intel Corporation

8:00am **HI+AS-ThM-1 Defect Engineering on the Atomic Scale with the Helium Ion Microscope*, Frances I. Allen,*** UC Berkeley **INVITED**

The use of ion beams to tune the properties of materials through the introduction of defects is a well-established technique. In this area, focused ion beam microscopes have the advantage that they allow the researcher to irradiate materials locally in a highly controlled manner. Over the last 15 years, the Helium Ion Microscope (HIM) has been employed for a range of defect engineering applications, in particular concerning thin films and 2D materials. Properties tuned include electrical, magnetic, optical and thermal behavior, achieved by varying the concentration of defects and local disorder, controlled by varying the ion dose [1]. In the case of freestanding atomic monolayer materials, it has been shown that irradiation with helium (and neon) ions using the HIM in raster mode (as opposed to e.g. spot mode), can form single vacancy defects and vacancy defect clusters due to single-ion hits [2,3]. Such sub-nanometer pores have applications in gas separation [4] and for selective ion transport in liquid [5]. In this talk, I will discuss the fabrication of sub-nanometer pores in 2D materials using the HIM. I will present characterization results from Raman spectroscopy and high-resolution transmission electron microscopy, and will also discuss the merits of multi-step fabrication workflows in which vacancy "seeds" are first introduced into the 2D material by ion irradiation, that are then expanded into the final nanopores of desired size and shape by plasma treatment and/or electron beam irradiation.

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8:40am **HI+AS-ThM-3 Effects of Defects and Si Doping on Ion Motion in TaOx Bilayer Memristors**, ***Matthew Flynn-Hepford,*** University of Tennessee Knoxville*; J. Keum, I. Kravchenko, S. Randolph, A. Ievlev, B. Sumpter,* Oak Ridge National Laboratory*; M. Marinella,* Arizona State University*; O. Ovchinnikova,* Oak Ridge National Laboratory

TaOx materials have promising properties for memristive applications such as long state retention time and consistent resistive switching.If the mechanism of the resistive switching can be controlled, these materials could be the foundation for the next generation of neuromorphic computing. A material design approach was implemented with the goal of lowering the operational voltage of these devices.Radial distribution functions (RDF) of the modeled TaOx materials with added defects and Si doping were used to predict the bonding strength of the materials.Experimentally, in order to increase ion mobility, defects were introduced into the active layer by He ion irradiation.Local strong bonding was induced in the form of local Si doping by Si irradiation, in an attempt to induce ion mobility channels where ion motion can be better controlled.In order to probe the mechanism of this resistive switching, conductive atomic force microscopy (c-AFM) and kelvin probe force microscopy (KPFM) were used to induce ion motion in the thin films and probe the change in surface potential, respectively.Specially resolved time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to probe the chemical change in the film with applied tip bias.These c-AFM and KPFM experiments along with ToF-SIMS were used to probe the locally defected and Si-irradiated areas in order to better understand the effects of defects and Si doping on ion mobility in TaOx bilayer memristors.

9:00am **HI+AS-ThM-4 Advantages of Using Helium Ion Microscopy for Morphological Analysis of BiScO$_3$-PbTiO$_3$ Piezoelectric Ceramics***, S. Chen, A. Bunevich, Y. Yuan,* ***Karen Kavanagh****, Z. Ye,* Simon Fraser University, Canada

Piezoelectric materials can convert mechanical energy into electrical and vice versa. Imaging by Scanning Electron Microscopy (SEM) is commonly used for initial morphological analysis of the grain size, uniformity and porosity, properties that correlate with the piezoelectric quality of interest. However, piezoelectric ceramic is highly insulating, requiring a conductive coating to inhibit charging while imaging through secondary electron collection in most SEMs. Thus, SEM images may not be representative of the sample surface. We have found that there are numerous advantages to using Helium Ion Microscopy (HIM) instead. In a HIM, a positively-charged focussed He ion beam is used to excite secondary electrons, with sample charging neutralized by a simultaneous, large-area electron flood gun. Samples are analysed directly without any surface modification, enabling rapid comparisons of a sintered batch for selection of the best quality ceramic for electrical testing. Higher resolution is achieved for better images of grain boundaries and textural irregularities that are not visible by SEM. In this talk, we will compare SEM and HIM secondary electron images of various compositions of BiScO$_3$-PbTiO$_3$ ceramics, a high temperature piezoelectric material. We will show examples of nanometer-wide ceramic grain boundaries and triple points that were not visible using SEM. Grain boundaries are regions of changes in the lattice structure that have significant implications for piezo and other electronic properties. We have found HIM images to show surface topography and regions of dramatically different contrast that are invisible in the SEM. Furthermore, the lack of conductive coating allows us to see variations in the grain boundary itself, which may explain why piezoelectric properties fluctuate with region in a single sample. Ceramics with large grains (> 20 mm) and flat surfaces correlated with high ferroelectricity at 200°C, with a P_{max} = 282 mC/cm^2. These samples were also more physically robust and able to be poled at higher temperatures and voltages than previous samples of the same composition, improving their piezoelectric properties. Incorporating HIM into the design and synthesis process allows us to quantify the effects of factors such as sintering temperature and die conditions on the physical quality of the ceramic, which ultimately determines its electronic properties and the feasibility of material commercialization.

Acknowledgments

This work is supported by the Natural Science and Engineering Research Council of Canada (NSERC grant RGPIN-2017-06915).

9:20am **HI+AS-ThM-5 Low-Energy Ion Implantation - Range Comparisons between Theory and Experiment***,* ***Michael Titze,*** Sandia National Laboratories*; J. Poplawsky,* Oak Ridge National Laboratory*; A. Belianinov, E. Bielejec,* Sandia National Laboratories

The continued decrease in size of microelectronic devices has created a need for shallower implanted dopant layers. With the recent discovery of two-dimensional (2D) materials, the ultimate limit for shallow layer implant is incorporating material into a single monolayer. Multi-specie focused ion beams (FIB) can operate with a variety of ion species and enable direct-write implantation of specific ions tailored for an exact application. Prior to any ion irradiation experiment, the range of ions in the material needs to be calculated, often predicted by using freely available Stopping and Range of Ions in Matter (SRIM) simulation.

SRIM simulations are in excellent agreement with experiment for high energy light ions, however, for low energy heavy ions, discrepancies between SRIM and observed experimental values have been reported. We use Rutherford backscattering spectrometry (RBS), Secondary ion mass spectrometry (SIMS) and Atom-probe tomography (APT) to measure the depth of heavy ions in silicon following FIB implantation with energies from 1 – 150 keV. The resolution limit of RBS and SIMS is on the order of nanometers, comparable to the implantation depth for few keV ion implants, requiring the use of APT for measuring lowest energy implants because APT is capable of almost angstrom resolution in the 100 direction of single crystalline Si. The difference between SRIM and experimental result is < 10 nm for all investigated ion energies, however due to the low overall range of the ions, the relative error is larger for lower ion energies with 1 keV as the minimum energy investigated showing > 500 % relative discrepancy.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE’s National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.APT research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

11:00am **HI+AS-ThM-10 Correlative Microscopy Using HIM and HIM/SIMS***,* ***Florian Vollnhals,*** Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; G. Sarau,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany*; A. Kraus,* Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; S. Christiansen,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany **INVITED**

The Helium Ion Microscope (HIM) has changed the world of charged particle microscopy [1]. The attainable spot sizes have enabled advances in imaging as well as nanotechnological applications such as ion beam lithography, nanopatterning or material modification.

An area that has been challenging for HIM, especially in comparison to scanning electron microscopy (SEM), is sample analysis beyond secondary electron (SE) imaging. While most SEMs are equipped with some form of X-ray detection systems (e.g., EDX) for chemical analysis, and many more analytical modes available for further characterization of physical or chemical sample properties, such capabilities have been limited for HIM [3].

The HIM community has made considerable efforts to improve this situation by introducing ion beam specific detection tools like Rutherford backscattering (RBS), Scanning Transmission Helium Ion Microscopy (STHIM) or Secondary Ion Mass Spectrometry (SIMS) using the neon ion beam provided by the latest generation ORION NanoFab HIM [2].

In HIM-SIMS, the focused ion beam is scanned across and thus sputters the surface, resulting in the emission of atoms and ions. The ions are collected and guided to a mass analyzer, allowing for the detection of ions and small clusters ranging from light elements like hydrogen, lithium and boron to heavy elements like Lead. Especially the detection of lithium is a valuable new tool for battery research.

Recently, the SIMS detection system developed by Wirtz et al. at Luxembourg Institute of Technology (LIST) has been upgraded from four individual detectors into a prototype focal plane detector within the npSCOPE project (npscope.eu, funded by the European Commission), allowing for the detection of many masses in parallel, which is beneficial for many applications for which a compositional analysis is required [3].

In addition to the detector development efforts at LIST, a focus has been set on the development of workflows for correlative microscopy using the HIM in a context of additional analytical modalities. The correlation of high resolution HIM and HIM-SIMS imaging with complementary analytical modalities like atomic force microscopy, optical or Raman microscopy to allow for new insights and overcome some of the limitations of the individual tools [4].

This contribution aims at showcasing applications of HIM-SIMS and offers some insights into correlative microscopy workflows involving the HIM.

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11:40am **HI+AS-ThM-12 Electronic vs. Nuclear Sputtering of Coronene**, ***Lars Breuer***, *T. Heckhoff, M. Herder,* University of Duisburg-Essen, Germany*; H. Tian, N. Winograd,* The Pennsylvania State University*; A. Wucher,* University of Duisburg-Essen, Germany

Electronic sputtering induced by swift heavy ion (SHI) irradiation of solids has been suggested as a relatively soft desorption mechanism for intact molecules in Secondary Ion Mass Spectrometry (SIMS). In order to evaluate the prospects of this “MeV-SIMS” technique as compared to the standard SIMS methodology utilizing nuclear sputtering with projectile energies in the keV range, we have performed a case study using time-of-flight (ToF) mass spectrometry to detect both ionized and neutral particles sputtered from a coronene film. In particular, secondary ion and neutral mass spectra obtained under 4.8 MeV/u Ca, Bi and Au ion impact were compared with those measured under irradiation with keV Ar, C_{60} and Ar_{1500} ions. While secondary ions were directly detected using a reflectron ToF spectrometer, sputtered neutral particles were post-ionized using two different laser photoionization schemes, namely vacuum ultraviolet single photon ionization at 157 nm and infrared strong field ionization at wavelengths between 800 and 1300 nm, respectively. The measured spectra are interpreted in terms of partial sputter yields, fragmentation patterns, emission velocity distributions and ionization probabilities with emphasis on the emission and/or formation of intact molecular ions.

The obtained data clearly demonstrate that the MeV-induced electronic sputtering process results in much cleaner molecule spectra than the keV-induced nuclear sputtering process even if cluster projectiles are used in the keV experiment. In particular for the Ca SHI and SPI post-ionization, the measured spectra are completely dominated by unfragmented neutral coronene molecules detected at m/z 300, followed by some fragmentation via the loss of one or more hydrogen atoms. Interestingly, the spectra measured under SHI impact are even cleaner than those measured under thermal evaporation conditions, thereby illustrating a fundamental difference between macroscopic thermal evaporation and the electronic sputtering process. Comparing the secondary neutral and ion spectra, one finds an ionization probability of the intact molecule of the order of 1 % under SHI impact, which may be slightly higher than that measured under keV C_{60}^+ ion impact (several 10^{-3}). Apart from the hugely different fragmentation characteristics, no significant difference is found between SHI and keV cluster ion impact regarding the emission velocity distributions of the emitted molecules, thereby indicating that the measured signals largely represent the respective partial sputter yields.

12:00pm **HI+AS-ThM-13 Scanning Transmission Helium Ion Microscopy-How Does It Compare to TEM?**, ***Annalena Wolff,*** Caltech*; R. Fieth,* QUT, Australia

This work explores the HIM’s analysis capabilities of unstained biological samples using a self-built dark field scanning transmission ion microscopy holder. For thin enough samples, such as thin sections of biological specimen on TEM grids, the high energy helium ions can penetrate through the sample. While the ion transverses through the thin foil, it undergoes collisions with the sample atoms and is deflected. The ion exits the sample at a deflection angle which is specimen thickness, ion energy as well as sample material dependent. The deflection angle can be determined using Monte Carlo simulations. The freeware program Stopping and Range of Ions in Matter was used in this work. This effect can be used to design a dark field scanning transmission ion microscopy holder (DF-STIM). The holder design is based on a previously reported experiment [1]. In principle, ions, which are deflected by a specific angle hit a metal conversion plate, which is mounted at a specified distance h below the sample. Here, the transmitted ions create a secondary electron signal which can be collected by the HIM’s Everhart-Thonley Detector. Ions which are deflected less than the acceptance angle enter a hole in the holder which his located directly below the specimen. This hole acts as a Faraday cup. For this case, no secondary electron signal is created. For biological samples, areas with higher carbon density create signal while areas with lower carbon density create less signal and can this be distinguished in the DF STIM image.

The DF STIM holder is tested by imaging stained and unstained biological samples and the results are compared to TEM measurements.

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[2] Dr. Crystal Cooper is thanked for the many useful discussions and the sample preparation suggestions.

Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More**, ***Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO$_2$ films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films***, **Vincent Ott**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated Cr$_{0.74}$Ta$_{0.26}$N Coating***, **Christina Kainz**,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated Cr$_{0.74}$Ta$_{0.26}$N coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–Cr$_{0.74}$Ta$_{0.26}$N solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. Cr$_{0.74}$Ta$_{0.26}$N powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-Cr$_{0.74}$Ta$_{0.26}$N to t–Cr$_{1.2}$Ta$_{0.8}$N sets in. Vacuum annealing of Cr$_{0.74}$Ta$_{0.26}$N on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-Cr$_{1.2}$Ta$_{0.8}$N at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–CrTaO$_4$ and r–Cr$_2$O$_3$ at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-Cr$_{0.74}$Ta$_{0.26}$N grains close to the substrate interface, a porous transition layer of r-Cr$_2$O$_3$ and t-CrTaO$_4$ and a dense r-Cr$_2$O$_3$ layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions***, **Nicholas D'Attilio**, F. Thompson, G. Crawford,* South Dakota School of Mines and Technology*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys***, **Jianliang Lin**,* Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy***, **Martin Dahlqvist**,* IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (MB$_2$) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes MB$_2$ coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron (B/M>2) [2] but the recent addition of understoichometic MB$_2$ coatings (B/M<2) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of MB$_2$, perfect match is found for M from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for M from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric MB$_2$. In our quest for improving the properties of MB$_2$ we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in MB$_2$. It will be shown how theory can be used to identify possible defects in MB$_2$ and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in MB_2 have a significant impact for *M* from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple MB_2 where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric MB_2 coatings.

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11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of $Ti_xZrNbTaFeB_y$ High Entropy Alloy Thin Films***, B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*; **Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB_2 nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder***, **Alessandro Troglia**, M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a charge-hopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

Surface Science Division
Room 319 - Session SS+AS-ThM

Memorial Session in Honor of Patricia Thiel II

Moderators: James Evans, Ames Laboratory, **Cynthia Jenks**, Oak Ridge Natinal Laboratory

8:20am **SS+AS-ThM-2 Navigating Complex Interfaces: In Memory of Patricia A. Thiel***, **Cynthia Jenks**,* Oak Ridge National Laboratory **INVITED**

At a time when simple systems in surface science were the norm, Professor Thiel would choose two paths for her research group. Part of the group focused on the seemingly simplistic and part of the group focused on the seemingly complex. A key to her success was not shying away from complexity or diving deep into the detailed mechanisms of what at first appeared simple, yet turned out to be anything but simple. Additionally, she garnered success by bringing together experts from different disciplines and backgrounds to tackle her research focus areas. Among the areas the group focused on from 1992 through 2008, when I worked with her, was on understanding the deposition of Ag on Ag and also on understanding the vast unknown of quasicrystalline surfaces with their all of their complexity. This talk will highlight some of the research during that time and how that work inspired a move toward understanding more complex interfaces in the field of surface science.

8:40am **SS+AS-ThM-3 Atomic Scale Investigation of Friction Properties of Quasicrystals and Beyond***, **Jeong Young Park**,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea **INVITED**

Quasicrystals that have rotational symmetry but no translational periodicity has been one of the key topics that Pat Thiel has explored and pioneered. Complex metallic alloys, including quasicrystals and approximants often have peculiar mechanical and tribological properties associated with the unique structure. For example, quasicrystals exhibit high hardness, low friction, and good wear resistance, prompting applications as anti-stick and low friction coatings. In this talk, I highlight the research efforts on nanomechanical and tribological properties of quasicrystal and approximant surfaces using atomic force microscopy. It was found that the friction response on twofold surfaces of the clean Al-Ni-Co decagonal quasicrystal where atoms are arranged periodically along the tenfold axis, and aperiodically in the perpendicular direction was anisotropic at different length scales (macroscale and nanoscale). The result indicates that there is an intrinsic relationship between the aperiodic atomic structure of quasicrystals and their low friction. On the oxidized surface and in the elastic regime, friction is dominated by the bulk properties of the metal beneath the oxide and is not sensitive to whether the metal is quasiperiodic or periodic. I discuss the role of the surface oxide and the length scale of mechanical contact in determining nanomechanical and tribological properties.

In the second part of my talk, I will highlight the recent investigation on the frictional behavior of intercalated water between the hydrophilic surfaces and more hydrophobic two-dimensional atomic layers. The water layers confined between the hydrophilic substrate and hydrophobic layers exhibit the bilayer structure that was proposed by Pat Thiel. We found that the water intercalated between 2-dimensional (2D) materials (e.g., graphene and MoS2) and the hydrophilic substrate increases the friction force between the AFM tip and 2D flakes deposited. Moreover, the friction on both graphene and MoS2 increased as the number of stacking water layers increased. This study provides that the intrinsic vibration modes of the water molecules play a key role in the coupling of the 2D materials modes to the phonon bath of the substrate. Finally, I will address the relationship between nanoscale friction on ultrananocrystalline diamond surface and the surrounding environment of water by using ambient pressure−atomic force microscopy. This result elucidates the role of vapor-phase water in the tribological properties of carbon-based materials.

9:20am **SS+AS-ThM-5 Quantification of Structure-Property Relationships at Interfaces*, Susan Sinnott,*** Pennsylvania State University **INVITED**

Many-body, dynamic charge, physics-based potentials are used in classical molecular dynamics (MD) simulations to investigate the chemistry associated with heterogenous systems. In particular, the interaction of graphene with titanium metal and titanium-carbide-derived-carbon (Ti-CDC) systems are investigated. The resulting Ti-CDC structures are then examined for the adsorption of acid gases. These findings illustrate the usefulness of classical MD simulations in designing new material systems.

9:40am **SS+AS-ThM-6 Metal Nodes in Bimetallic Metal-Organic Frameworks as Isolated Sites for Gas-Phase Catalytic Hydrogenation*, Donna Chen,*** University of South Carolina **INVITED**

The $Cu_xRh_{3-x}(BTC)_2$ catalyst (abbreviated CuRhBTC, BTC^{3-} = benzene tricarboxylate) provides excellent dispersion of active metal sites coupled with well-defined, robust structures for propylene hydrogenation reactions.This material therefore serves as a unique prototype for understanding gas-phase catalytic activity in metal organic frameworks (MOFs). The active sites for hydrogenation are identified as Rh^{2+}, while role of Cu^{2+} is primarily to provide stability for the MOF structure. In situ XRD studies show that the crystalline MOF structure is retained during hydrogenation.The appearance of the O-H stretch for COOH at ~3690 cm^{-1} in the diffuse reflectance infrared Fourier transform spectra is characteristic of defects consisting of missing Rh-O bonds. These experimental results are consistent with the reaction mechanism proposed by density functional theory, in which H_2 is dissociated at a Rh^{2+} site with a missing Rh-O bond, while protonation of the decoordinated carboxylate linker stabilizes the active sites and promotes H_2 dissociation.

11:00am **SS+AS-ThM-10 Quasicrystals in Two Dimensions: From Metals To Molecules And Oxides*, Vincent Fournée,*** Institut Jean Lamour - CNRS-Université de Lorraine, France **INVITED**

Quasiperiodic structures exhibit long-range order like normal crystals but they lack translational symmetry. Quasicrystals were first discovered as a new class of intermetallic compounds, now comprising hundreds of members in binary and ternary systems. They usually adopt either the icosahedral or the decagonal point group symmetry. The discovery of quasicrystals has led to a paradigm shift in crystallography and has attracted a large interest in the material science community, motivated by unexpected physical properties that could be linked to quasiperiodicity. This remarkable class of materials has also challenged our understanding of metal surfaces. An atomic scale description of their surfaces is especially important, as it forms the basis for understanding and predicting phenomena such as gas adsorption, metal epitaxy, and friction. Pat Thiel and her group played a major role in the surface science of quasicrystals.

Pat Thiel also pioneered studies of nucleation and growth of metal thin films on quasicrystalline surfaces, demonstrating that local pseudomorphic growth can occur due to preferred adsorption of the metal ad-species at specific sites of the surface quasilattice. The idea was that the complex potential energy surface of quasicrystalline surfaces could serve as a template to grow new 2D quasicrystalline systems.

Here, we will review the different results obtained along this direction, from local peudomorphic growth of Al starfish islands on the 5-fold surface of the icosahedral *i*-Al-Cu-Fe quasicrystal [1] to pseudomorphic single layer high islands in the case of Ag/5f-Al-Pd-Mn [2] and up to the formation of complete 2D quasiperiodic metal layers (Pb, Bi or Sn) templated on various quasicrystalline surfaces [3]. Self-organized molecular films with long-range quasiperiodic order could also been grown by using the complex potential energy landscape of quasicrystalline surfaces as templates. The long-range order arises from a specific subset of quasilattice sites acting as preferred adsorption sites for the molecules, thus enforcing a quasiperiodic structure in the film [4]. Finally we will show some recent examples of 2D quasicrystalline oxide layers obtained by reduction of ABO_3 perovskite thin films grown on Pt(111) [5,6].

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11:40am **SS+AS-ThM-12 Unusual Flat and Extended Morphology of Intercalated Cu Under MoS_2*, Dapeng Jing,*** *Y. Han, J. Evans, M. Kolmer, Z. Fei, M. Tringides,* Ames Laboratory USDOE **INVITED**

There has been intensive research on ultra-thin metal films and surface structures for use as transparent conductor layers in optical and thermal applications. In this study, we present a novel approach to fabricate such metal structures of Cu encapsulated near the surface of a layered material, MoS_2. We use scanning electron microscopy, atomic force microscopy and x-ray photoelectron spectroscopy to characterize this Cu-MoS_2 system formed via physical vapor deposition of Cu in ultrahigh vacuum at 1000 K. Necessary conditions for encapsulation are preexisting ion-induced defects in the MoS_2 substrate and elevated deposition temperature of 1000 K. Under such conditions, Cu grows both on the MoS_2 surface as facetted clusters and beneath the MoS_2 surface as encapsulated structures. The encapsulated Cu starts underneath a surface cluster and grow laterally in size maintaining a thickness of under 10 nm. The Cu structure growth behavior deviates significantly from the Cu intercalation in graphite system where Cu predominantly grows as intercalated islands with much smaller lateral size. Density functional theory calculations reveal the driving force for Cu mass transport from surface clusters to encapsulated structures.

12:00pm **SS+AS-ThM-13 Helium Ion Microscopy for Surface Modification and Characterization*, Alex Belianinov,*** Sandia National Laboratory **INVITED**

There is a growing need to expand the experimental arsenal with tools to visualize and modify materials at a breadth of scales, from atomic to visible with a naked eye. The helium ion microscope (HIM) offers a large dynamic range, and quickly gained popularity since its debut in 2006. Its unique gas field ion source (GFIS) is ideal for high-resolution imaging, milling, localized damage, direct-write, and additional analytical techniques like secondary ion mass spectrometry as well as ion beam induced current imaging.

This presentation aims at providing an overview of the status of HIM technology for imaging, analysis, and nanofabrication. Specifically, the instrument design, ion-matter interaction, imaging, localized material modification, and material characterization will be discussed. Contrast will be drawn between the HIM and other focused ion beam tools in this class that rely on liquid metal alloy ion sources. Current challenges and research opportunities for ion beam tools will be highlighted. A plethora of supporting examples of working with 2D, cleanroom-relevant, soft, polymeric, and biological materials will be shown.

This presentation is dedicated to my mentor and advisor Prof. Patricia A. Thiel. She lives on through the memories of all of us that were lucky enough to spend time with her.

Acknowledgement

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2D Materials Technical Group
Room 303 - Session 2D+AS+EM-ThA

2D Materials: Electron Microscopy and Photoemission Spectroscopy

Moderators: Keun Su Kim, Yonsei University, Republic of Korea, **Dmitry Kireev**, University of Texas at Austin

2:20pm **2D+AS+EM-ThA-1 Periodic Lattice Displacements in Low Dimensional Materials***, **Robert Hovden,*** University of Michigan **INVITED**

Dramatic electronic changes are associated with periodic lattice displacements [1] where structure, even in 2D materials, requires higher dimensional measurement using scanning / transmission electron microscopy. In particular charge density waves are an emergent periodic modulation of the electron density that permeates a crystal with strong electron-lattice coupling. Strong evidence suggests that transformative correlated electron behavior may exist only in unrealized clean 2D materials such as 1T-TaS_2. Unfortunately, experiment and theory suggest that extrinsic disorder in free standing 2D layers impedes correlation-driven quantum behavior. Here we demonstrate a new route to realizing fragile 2D quantum states through epitaxial polytype engineering of van der Waals materials. The isolation of truly 2D charge density waves (CDWs) between metallic layers stabilizes commensurate long-range order and lifts the coupling between neighboring CDW layers to restore mirror symmetries via interlayer CDW twinning. The twinned-commensurate (tC-) CDW reported herein has a single metal–insulator phase transition at ~350 K as measured structurally and electronically [2]. Fast in-situ transmission electron microscopy and scanned nanobeam diffraction map the formation of tC-CDWs. This work introduces epitaxial polytype engineering of van der Waals materials to access latent 2D ground states distinct from conventional 2D fabrication.

Here we show the critical temperature for spatially-coherent, commensurate (C-) CDW in 1T-TaS_2 can be raised to well above room temperature (~150 K above the expected transition) by synthesizing clean interleaved 2D polytypic heterostructures. This stabilizes a collective insulating ground state (i.e. C-CDW) not expected to exist at room temperature. We show the formation of these spatially coherent states occurs when 2D CDWs are confined between metallic prismatic polytypes. At the same time, interleaving disables interlayer coupling between CDWs. This raises the critical temperature of the C-CDW and forms out-of-plane twinned commensurate (tC) CDWs as revealed by scanned nanobeam electron diffraction. These results demonstrate polytype engineering as a route to isolating 2D collective quantum states in a well-defined extrinsic environment with identical chemistry but distinct band structure.

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[2] *Two-dimensional charge order stabilized in clean polytype heterostructures*, S. H. Sung et al. **Nature Communications**, **13** 413 (2022)

3:00pm **2D+AS+EM-ThA-3 Engineering of Nanoscale Heterogenous Transition Metal Dichalcogenide-Au Interfaces***, **Alex Boehm,*** Sandia National Laboratories*; J. Fonseca,* Naval Research Laboratory*; K. Thuermer, J. Sugar,* Sandia National Laboratories*; J. Robinson,* Naval Research Laboratory*; T. Ohta,* Sandia National Laboratories

2-D transition metal dichalcogenides (TMDs) have recently garnered much attention owing to their extraordinary physical, chemical, electrical, and optical properties. However, early material and device studies have revealed that these properties can be greatly impacted by extrinsic factors such as substrate interactions, mechanical strain, and charge transfer. Thus, a careful understanding of the nuanced interactions between TMDs and other materials is critical for high performance devices. Of particular importance are the interfaces with metallic contacts. Here, one barrier are the spatial nonuniformities recently reported at these types of interfaces. Uncovering the impact of these heterogeneities on TMD properties and establishing strategies to control TMD-metal interfaces could enable an array of engineering pathways for future applications. In this work, we find that the electronic structures of mechanically exfoliated TMD-Au interfaces exhibit pronounced heterogeneity arising from microstructure of the supporting metal. Pertinent for device applications these electronic structure variations indicate fluctuating doping levels and Schottky barrier height across the junction. We examined the electronic structures of WS2 and WSe2 at high spatial resolution via photoemission electron microscopy (PEEM) revealing key differences in work function and binding energies of the occupied states. Furthermore, the inherent role of the underlying Au microstructure on the TMD electronic structure is revealed by electron backscatter diffraction (EBSD) and scanning tunneling microscopy (STM). Finally, simple processing methods are employed to fabricate homogenous TMD-Au interfaces while also tuning the electronic properties of the TMDs. Our findings illustrate that the electronic properties of TMDs are greatly impacted by metal interface interaction and provide a means to engineer these important junctions.

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3:20pm **2D+AS+EM-ThA-4 Advanced Laboratory-Based Momentum Microscopy and PEEM Analysis***, **Stefan Böttcher Böttcher,*** SPECS Surface Nano Analysis GmbH, Germany*; D. Singh, T. Conard,* IMEC, Belgium*; M. Wietstruck,* SPECS Surface Nano Analysis GmbH, Germany*; P. van der Heide,* IMEC, Belgium*; A. Thissen,* SPECS Surface Nano Analysis GmbH, Belgium

Momentum Microscopy is a new technology for comprehensive surface analysis, providing high energy and angular resolved band structure mapping combined with advanced surface imaging capability. Extending this technology with laboratory-based instrumentation opens the possibility for detailed studies of new materials under well controlled environments. The combination of a PEEM lens for surface microscopy and momentum microscopy, allows for small spot analysis in ARPES and chemical sensitive surface mapping. In a joint project between IMEC and SPECS the possibilities for laboratory-based momentum microscopy, laser ARPES and x-ray spectroscopy and microscopy are evaluated in the framework of semi-industrial environment. We present a status report at the intersection between fundamental and applied research in surface science. We focus on the use of ARPES characterization in novel materials close to applied research and the functionality of x-ray analysis in PEEM and spectroscopy for chemical analysis.

3:40pm **2D+AS+EM-ThA-5 Epitaxial Growth and Electronic States of Ultrathin Bi (111) Films on Insb (111)B: Evidence of Inversion Symmetry Breaking via Film-Substrate Interactions***, **Hadass S. Inbar**, J. Dong, A. Engel, C. Dempsey, Y. Chang,* University of California Santa Barbara*; A. Fedorov,* Advanced Light Source, Lawrence Berkeley National Laboratory*; C. Palmstrom,* University of California Santa Barbara

Quantum size effects in bismuth films have been the focus of the scientific community for decades. The spin–split Rashba surface states and large mass anisotropy in surface state valleys have made Bi films a promising system for future applications in spintronics and valleytronics. Moreover, in the field of topological materials, the Bi (111) bilayer (BL) is predicted to behave as a quantum Hall spin insulator[1]. Along the Bi (111) step edges, 1D helical modes were observed[2], an ingredient in one proposed platform to construct Majorana zero modes[3]. However, the synthesis of continuous ultrathin (<6 BL) Bi (111) epitaxial films on semiconducting substrates has remained a materials challenge. We report a study of ultrathin large-area Bi (111) layers grown on InSb (111)B substrates by molecular beam epitaxy and in-vacuo transferred for scanning tunneling microscopy and synchrotron-based angle-resolved photoemission spectroscopy. We show that large-area single-domain ultrathin Bi films can be stabilized through strong film-substrate interactions. Our study follows the evolution of tensile strain in the films, which is predicted to lead to a semimetallic to semiconducting transition. With decreasing film thickness from 13 to 1 BL, we quantify the confinement-induced shifts in the bulk band structure and trace the quantum well energy levels with a phase shift accumulation model. Significant substrate-film interactions breaking inversion symmetry affect the surface state dispersion leading to a surface state degeneracy which allows us to assign the topological order in Bi(111) thin films. The findings of this study offer a new route for epitaxial growth and integration of band-engineered Bi films with III-V substrates.

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4:00pm **2D+AS+EM-ThA-6 Band Modulations: Revealing Moiré Effects in Twisted Bilayer 2D Materials**, ***Ryan Muzzio,*** Carnegie Mellon University; *A. Jones, P. Majchrzak,* Aarhus University, Denmark; *H. Martins, S. Singh,* Carnegie Mellon University; *C. Jozwiak, A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory; *P. Hofmann,* Aarhus University, Denmark; *S. Ulstrup,* aarhus University, Denmark; *J. Katoch,* Carnegie Mellon University

Two dimensional (2D) materials are a wonderful template to explore novel quantum phenomena in the ultra thin limit.They can be exfoliated to the desired thickness, stacked with other 2D flakes, and be integrated in device fabrication for electrical measurement.The addition of a twist angle between stacked 2D flakes produces a moiré lattice which can lead to drastic changes in their physical properties.For the case of bilayer graphene, introducing a ~1.1 degree rotation (the magic angle) leads to a low temperature superconducting state[1].This remarkable transport result has been explained via band structure theory and experiment[2,3,4] of the hybridization of the out-of-plane Pi orbitals of the graphene layers which forma weakly dispersing state at the fermi level.Beyond graphene, twist-angle dependent bilayer transition metal dichalcogenides (TMDCs) also display extraordinary novel moiré physics[5,6].In this presentation, we will discuss our ongoing analysis of nano- and micro-focused angle resolved photoemission spectroscopy (ARPES) performed on twisted bilayer graphene and TMDCs systems placed on hBN.We demonstrate, over a wide range of twist angles, the effect of the moiré lattice and proximity effects on the band structure by investigating the effective masses, band positionings, and location of the moiré bands across four TMDC heterobilayers.Our work demonstrates the tunability of the electronic properties in twisted 2D bilayers and the power of ARPES to provide a momentum-resolved view of their electronic structure.

Applied Surface Science Division
Room 320 - Session AS+2D+EM+MS+NS+SS+TF-ThA

Probing Defects at Surfaces and Interfaces

Moderators: Michaeleen Pacholski, The Dow Chemical Company, **Zachary Robinson**, SUNY Brockport

2:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-1 Controlling InP Quantum Dot Surface Defects Using ALD-inspired Surface Chemistry and Phosphorus Kα and Kβ X-ray Emission Spectroscopy**, ***Nayon Park,*** University of Washington **INVITED**

Colloidal InP quantum dots are a leading heavy-metal-free semiconductor material for spectral downconversion in current generation display technologies and future generation energy efficient LEDs. Achieving the brightest and narrowest photoluminescence (PL) relies on the synthesis of structurally and electronically defect-free quantum dots. InP quantum dots' high propensity for oxidation and the inherent oxidative defects arising from commonly used synthesis methods therefore motivates a systematic approach to probe InP oxidation as a function of synthesis and surface treatments and correlation with the resultant optical properties. Phosphorus X-ray Emission Spectroscopy (XES) presents itself as an exceptional tool in this regard. In this talk, I will show recent results from computational modeling where we find that native InP surface oxides give rise to dark states near the band edge. Replacing the surface indium with zinc to form a monolayer ZnO shell results in the reduction of dark states. Using ALD-inspired successive ionic layer adsorption and reaction (SILAR), we developed the colloidal, layer-by-layer growth strategy of metal oxide shells (i.e. ZnO, CdO, GaO_x, AlO_x) on InP quantum dots at room temperature using common ALD precursors (*i.e.*, metal alkyls and water). Metal oxide-shelled InP QDs generally show enhanced PL and evidence of bulk and local structural perturbations arising from the metal oxide as determined by X-ray diffraction and X-ray absorption spectroscopy. Further, we explore the impact of these metal oxide interfaces on the PL QY and emission linewidth of InP/ZnSe core/shell QDs. Upon growing a thin ZnSe shell, we observe improved PL properties, which we hypothesize to be attributable to the inhibition of phosphorus migration to the shell due to the presence of the metal oxide interlayer, as supported by X-ray emission spectroscopy. Taken together, these results suggest a clear path forward in the control and design of complex QD interfaces with atomistic insight for optoelectronic technologies.

3:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-3 Characterization of MAX Phases using a Combination of Micro-spot XPS, HAXPES and C60 Cluster Depth Profiling**, ***Kateryna Artyushkova,*** Physical Electronics USA; *M. Anayee, Y. Gogotsi,* Drexel University

Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) have seen significant increases in the number of research areas and publications. MXenes have a unique combination of properties that have led to many applications.[1] MXenes are usually synthesized by etching "A" layers that interleave "MX" layers in the bulk MAX precursors. MAX are represented by Mn+1AXn, where M denotes early transition-metals (Ti, V, Cr, Mo, etc.), X is N or C, and A is an A-group element such as Al, Si and others. During synthesis, impurities and defects may be introduced, which significantly impact the properties of the resulting materials. It is therefore critical to detect and quantify these defects and impurities.

X-ray Photoelectron Spectroscopy (XPS) has the advantages of being easily quantifiable and providing chemical information such as surface termination and oxidation. However, there are many challenges in using XPS for analyzing MAX and Mxene. The first is a very small size of MAX, less than a few tens of microns. With the development of focused scanning micro-probe X-rays, these limitations can be overcome. The other challenge is the extreme surface sensitivity of XPS. It is challenging to separate surface adventitious carbon and oxygen from possible oxygen incorporation in the carbon site. Depth profiling using a monatomic Ar ion beam is not suitable as it can introduce damage to the structure of MAX.

In this work, we are presenting two approaches to address this challenge. The first involves the application of Hard X-ray Photoelectron Spectroscopy (HAXPES), in which a monochromated Cr X-ray source is used to probe ~3 times deeper than a soft Al X-ray. The second utilizes a cluster ion gun source, such as C60, for damage-free depth profiling through individual MAX particles using ~8µm X-ray spot for probing if oxygen is present in the MAX structure.

3:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-4 Unusual Trend in Thermal Stability of Alanine Different Ni Surfaces**, *J. Ontaneda,* Queen Mary University of London, UK; *R. Grau-Crespo,* University of Reading, UK; ***Georg Held,*** Diamond Light Source, UK

Chirally modified heterogeneous catalysts promise massive savings of cost and toxic waste in the production of enantiopure precursors for high-value chemicals such as pharmaceuticals, fertilizers, or fragrants [1]. A key aspect is the thermal stability of chiral modifiers, which generally are chiral organic molecules bound to a chemically active metal surface. The enantioselective hydrogenation of methylacteoacteate (MAA) is a topical reaction, which is catalysed by nickel modified with chiral carboxylic acids, such as alanine, tartaric acid, or aspartic acid [2]. The components of this catalytic system have been investigated using various surface sensitive techniques [3,4,5]. Here we present a study of the thermal stability of alanine on the three most common Ni surfaces, {111}, {100}, and {110}, using synchrotron-based temperature-programmed photoelectron spectroscopy and X-ray absorption spectroscopy. In contrast to common experience with smaller molecules, alanine is more stable on the more open {110} and {100} surfaces compared to {111}. Comparison with a detailed DFT study identifies structural and electronic effects that play a role in this unusual behaviour.

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3:40pm **AS+2D+EM+MS+NS+SS+TF-ThA-5 Correlative Theoretical and Experimental Study of the PC | X Interfacial Bond Formation (X = TiN, AlN, TiAlN) During DC Magnetron Sputtering**, ***Lena Patterer,*** *P. Ondračka, D. Bogdanovski, S. Karimi Aghda, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Due to their outstanding oxidation and wear resistance, cubic (Ti,Al)N is widely used as protective coatings on forming and cutting tools. These characteristics make (Ti,Al)N also an attractive candidate for the protection of polymer components. The composition-induced changes in the interfacial bond formation of DC magnetron sputtered TiN, AlN, and $Ti_{0.25}Al_{0.25}N_{0.5}$ onto polycarbonate (PC) substrates are systematically investigated by correlating theory and experiment. In order to simulate the sputtering condition by *ab initio* molecular dynamics, a periodic structural model of bulk PC consisting of 394 atoms was bombarded by several Ti, Al, and N atoms with a kinetic energy of 1 eV. While both Ti and N atoms show high reactivity towards all functional groups of the polymer during the surface bombardment, Al atoms selectively react only with the carbonate group of PC or other reactive functional groups that have formed during previous bombardment events (e.g. C-N groups). At the PC | TiN and PC | TiAlN interfaces, Ti and N contribute equally to the interfacial bond formation, whereas the PC | AlN interface is defined mostly by C–N groups with Al-rich clusters forming on top of these groups. X–ray photoelectron spectroscopy data of the PC | X interfaces (X = TiN, AlN, TiAlN) show a very good agreement with the above-discussed predictions as the formation of C-N, C-(Ti,Al), and (C–O)–(Ti,Al) bonds is experimentally verified. This shows that the here employed computational strategy enables predictions of the interfacial bond formation between polycarbonate and metal nitrides, and it is reasonable to assume that the here proposed research strategy can be readily adapted to other polymer | inorganic material interfaces.

4:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-6 Using Resonant Photoemission Spectroscopy to Probe the Electronic Structure of Complex Oxides with Elemental and Orbital Specificity***, **Jessica McChesney**, D. Fong, H. Hong,* Argonne National Laboratory, USA

Understanding the role of defects and interfaces is necessary in order to realize many of the promising novel properties of complex oxide heterostructure devices. To this aim, we employ resonant angle-resolved photoemission spectroscopy to probe the electronic structure with elemental and orbital specificity of complex oxide heterostructure $LaTiO_3/SrTiO_3$ (LTO/STO).Combining these spectroscopy measurements with in-situ growth characterization we are able to determine the minimum thickness required to achieve high quality heterostructures with abrupt interfaces and to correlate the formation with the 2DEG with the interface termination LTO/STO vs STO/LTO.In addition, we explore the role of oxygen vacancies in formation of the 2DEG on the bare substrate and reveal that contrary to expectations, the 2DEG is Ti^{4+} in character while the oxygen defects are Ti^{3+} in character.

Electronic Materials and Photonics Division
Room 304 - Session EM+AS+EL+NS+SS-ThA

Interfaces and Defect Engineering in Electronic & Photonic Materials & Devices

Moderator: Erin Cleveland, U.S. Naval Research Laboratory

2:20pm **EM+AS+EL+NS+SS-ThA-1 Design and Control of Defect-Mediated Properties in Electronic Ceramics***, **Elizabeth Dickey**,* Carnegie Mellon University **INVITED**

Crystalline lattice defects, e.g. vacancies, interstitials or substitutional ions, play an important role in the conductivity and dielectric properties of electronic ceramics. The material “defect chemistry” can be tuned to optimize the electronic and ionic conductivities for particular applications via doping, oxygen-activity and temperature control during processing. Beyond controlling the majority defect (carrier) concentrations, it is also important to control the minority defect concentrations as these can be especially relevant to the time-dependent electrical behavior. For example, applied electric fields in device applications provide a strong driving force for the electromigration of charged lattice defects. Furthermore, external conditions such as humidity, which can lead to proton incorporation, can also strongly influence time-dependent material properties. This talk will review our current understanding and implications of point defect equilibria, partial equilibria and dynamics in several prototypical electronic ceramics. Recent efforts to effectively co-dope dielectric materials to improve simultaneously limit both the electronic and ionic conductivity will be discussed.

3:00pm **EM+AS+EL+NS+SS-ThA-3 In-Situ Investigation of the Interface Formation between Si-Terminated Diamond and a NbxOy Electron Acceptor Layer for Electronic Applications***, **Gabrielle Abad**, P. Hopkins, S. McDonnell,* University of Virginia

Ultra-wide band gap semiconductors present one avenue for the next generation of semiconductor devices. Diamond, specifically, has shown promise in high power, frequency, and temperature electronics; however, issues with impurity doping has limited the development of diamond-based devices. Instead, surface charge transfer doping (SCTD), which avoids introduction of foreign atoms into the diamond lattice, has been used for inducing a two-dimensional hole gas at the diamond surface thus increasing its conductivity. The established method to achieve SCTD is to hydrogen-terminate the diamond surface prior to the addition of an electron acceptor layer; however, the degree of SCTD induced by H-termination is largely dependent on atmospheric exposure. Alternatively, silicon-termination of the diamond surface has been shown to produce the ordered surface with the negative electron affinity necessary for the SCTD mechanism. In this work, we investigate the combination of Si-terminated diamond with a Nb_xO_y electron acceptor layer, wherein we focus on understanding interface formation and chemistries, as well as elucidating if the band alignment mechanism is responsible for SCTD for this material system. Ultra-high vacuum (UHV) electron beam (e-beam) deposition of Si onto diamond substrates was carried out, followed by UHV annealing to produce the Si-terminated (100) diamond surface. X-ray photoemission spectroscopy (XPS) of core-level and valence band spectra was used to analyze chemical composition. To form the electron acceptor layer, Nb films were e-beam deposited onto the Si-terminated diamond surface by depositing Nb under varying oxygen partial pressures. XPS was used to observe how interfacial chemistry, electronic structure, and band alignment evolve with different Nb_xO_y compositions. The air stability of the electron acceptor layers was also investigated after atmospheric exposure via XPS. Analysis of the valence band spectra shows that band alignment would not result in SCTD for the Nb_xO_y/Si/diamond material system.

3:20pm **EM+AS+EL+NS+SS-ThA-4 Effects of Atmospheric UV-O_3 Exposure of WSe_2 on the Properties of the HfO_2/WSe_2 Interface***, **Maria Gabriela Sales**,* University of Virginia*; A. Mazzoni,* University of Maryland College Park*; W. Sarney,* Army Research Laboratory*; J. Pearson,* University of Maryland College Park*; S. Najmaei,* Army Research Laboratory*; S. McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDCs) are a class of two-dimensional (2D) layered materials, in which each layer is held in-plane by strong chemical bonds, but held in the out-of-plane direction by weak van der Waals forces. For integration in an electronic device, TMDCs are typically capped in the gate region with a high-quality dielectric layer, where ultrathin (sub-5 nm) dielectric thicknesses are desired in order to achieve sufficient gate to channel electrostatic coupling. The unreactive basal plane of TMDCs makes atomic layer deposition (ALD) of dielectric films directly on top of these 2D materials challenging. In this work, we investigate the effects of atmospheric ultraviolet-ozone (UV-O_3) exposures of WSe_2 and use the UV-O_3 functionalized WSe_2 surfaces as substrates for ALD of HfO_2. We report two UV-O_3 functionalization regimes observed on WSe_2: lower exposure times, which do not result in oxidation of the WSe_2 surface, and higher exposure times, which result in a tungsten oxyselenide top layer. The properties of this oxidized layer, such as its thickness, structure, air stability, and thermal stability, are also investigated. Additionally, we note that both functionalization regimes result in variably doped WSe_2. We report on the interface chemistry observed after subsequent ALD of HfO_2, as measured with X-ray photoelectron spectroscopy (XPS). We note that variable, depth-sensitive doping states are found in the WSe_2 functionalized with higher exposure times. We also study the resultant morphologies of our deposited HfO_2 films with atomic force microscopy (AFM), and we find that both of our UV-O_3 functionalization regimes result in uniform and smooth HfO_2 films directly deposited by ALD. With the different functionalization regimes (with different interface chemistries) all providing uniform dielectric film deposition, our atmospheric UV-O_3 exposure technique on WSe_2 presents unique tunability and flexibility in the design of interfaces in devices.

3:40pm **EM+AS+EL+NS+SS-ThA-5 Near Zero Field Magnetoresistance and Electrically Detected Magnetic Resonance Studies of Instabilities in Semiconductor/ Insulator Systems***, **Patrick Lenahan**,* Pennsylvania State University **INVITED**

We have utilized both electrically detected magnetic resonance(EDMR) and near zero field magnetoresistance (NZFMR) spectroscopy to investigate the physics involved in instabilities such as stress induced leakage currents and time dependent dielectric breakdown in Si/SiO_2 and SiC/ SiO_2 systems. Both techniques are extremely sensitive and extend the sensitivity of conventional electron spin based techniques down to near nanoscale device structures. We find that the very simple spin-based NZFMR technique has significant analytical power in these investigations. The NZFMR studies can complement the more established EDMR measurements with simple and relatively inexpensive apparatus.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+NS+SS-ThA

Special Session and Reception for the HC Community and to Celebrate Robert Madix

Moderators: Liney Arnadottir, Oregon State University, **Dan Killelea**, Loyola University Chicago, **Jason Weaver**, University of Florida

2:20pm **HC+AS+NS+SS-ThA-1 Gaede-Langmuir Award Talk: Not a Divide - A Continuum: Surface Science to Heterogeneous Catalysis***, **Robert J. Madix**[1],* Harvard University **INVITED**

The science of surface reactivity demands control of surface structure and surface composition. Surface science methods thus enable the investigation of reactions, including oxidations, hydrogenation, and coupling, on well-characterized single-crystal surfaces by providing molecular level insight into the bond breaking and formation on surfaces that are the basis for heterogeneously catalysis. The ultimate goal of such research is to provide benchmarks for theory, forming a firm basis for *a priori* catalyst design. In the nearer term it provides a kernel of information which can be combined with theory to accurately predict rates and selectivities for extended series of analogous reactions outside the data set. In this talk, these concepts will be discussed, linking fundamental surface science studies on Au single crystals with the performance of dilute Au-based dilute metal alloy catalysts operating at elevated temperature and 1 atm pressure. The use of key surface-science methods, including XPS, vibrational spectroscopy and temperature programmed reaction spectroscopy, will illustrate the methodology for understanding catalytic reactions. This work demonstrates the ability to successfully predict surface reactivity across vast regimes of pressure, temperature and materials complexity.

Advanced Surface Engineering Division
Room 317 - Session SE+AS+MN+SS-ThA

Mechanical and Tribological Properties of Thin Films and Coatings

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

3:00pm **SE+AS+MN+SS-ThA-3 Differential Impact of Scale Dependent Roughness on Lubricant Infused Surfaces***, **Robert Chrostowski**, B. Fang, J. Smith, F. Mangolini,* University of Texas at Austin

Lubricant Infused Surfaces (LIS), which consist of an engineered surface texture with an absorbed lubricant, have recently emerged as an innovative approach for achieving pressure-stable omniphobicity and for improving tribological performance in the presence of external contaminants. The design of successful LIS heavily relies on the effect of surface texture, which is quantified using a single dimensionless parameter, namely the ratio of the true surface area to the nominal surface area. Previous published studies have thus focused on the evaluation and optimization of microscale pattered morphologies with simple geometries (for which the ratio of the true surface area to the nominal surface area can be determined analytically), such as ordered arrays of pillars. Texture, however, is defined both by these larger-scale structures, and by smaller sub-micron scale asperities called roughness. Roughness can exhibit scale-dependent fractal self-similarity, and the absolute finest scales of roughness can have outsize impact on the quantitative value of the area ratio. Despite the scientific relevance of previous studies on fractal surfaces and the effect of roughness on contact mechanics, our understanding of the effect of surface roughness on the retention of a lubricant is elusive.

Here, we evaluate the lubricant infusion behavior of two different fluorinated polymer lubricants of substantially different molecular size, but similar surface chemistry, on fractal nano-rough boehmitized aluminum surfaces. Power spectral density (PSD) analysis of atomic force microscopy (AFM) topography maps is used to estimate the area ratio for each surface at the length scale of the radius of gyration of the different lubricants. The area ratio values computed from the PSD are then related to true area value that matches predicted spin-coating curves to observed gravimetric ones. The experimental results demonstrate, for the first time, the impact of fractal roughness on the shear-retention of LIS. The outcomes of this work, providing evidence that different molecular length fluids could experience different quantitative magnitudes of roughness on the same, significantly contribute to our understanding of the impact of scale-dependent roughness on the retention of liquids on engineered surface textures, while enhancing the scalability of LIS systems and their cost-effective implementation in several technological applications.

3:20pm **SE+AS+MN+SS-ThA-4 Imperfectly Perfect Coatings for Rolling Bearing Applications***, **Esteban Broitman**,* SKF B.V. - Research and Technology Development, Netherlands **INVITED**

Machines with rotating components usually rely on bearings to reduce friction in moving its parts around a fixed axis. The increasing demand for more precise bearings to lower power consumption and heat generation, while simultaneously support increasing applied loads and/or higher speeds, has given place to the use of surface engineering processes.

In the case of bearings, it is widely accepted the advantages of using coatings as the surface process to improve its performance. During the last three decades, advanced coatings have enjoyed a growing interest in several industrial applications because they can be engineered to provide different properties like electrical insulation, low friction, and resistance to corrosion, plastic deformation, etc.

In this talk I will compare the structural, mechanical and tribological properties of two coatings that are used nowadays to improve the performance of rolling bearings made of standard bearing steel: they provide lower friction, resistance to surface initiated rolling contact fatigue, and decreased wear: NoWear® (a carbon-based nanostructured coating made by plasma-assisted chemical vapor deposition PACVD) of about 3 µm-thick, and Black Oxide (an iron oxide film made by a chemical conversion method) of about 1 µm-thick. Being coatings produced by different techniques, both have a common feature: they are *"imperfectly perfect coatings."* Scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation measurements show that, from the microstructural point of view, these coatings are full of *"imperfect"* features, like cracks, voids, porous, columns, and other naughty irregularities. The different mechanisms contributing to the positive tribological behavior of each coating under lubricated conditions will be discussed. I will demonstrate that these coatings, taking advantage of their own different *"imperfect"* features, behave *"perfectly"* from the tribological point of view, and therefore can successfully be used to extend maintenance and life expectancy of specialized rolling bearings.

4:00pm **SE+AS+MN+SS-ThA-6 Tribological Behavior of WC/WCN/CNx Thin Films Deposited by HIPIMS***, **Luis Flores-Cova**, O. Jimenez, M. Flores,* Universidad de Guadalajara, Mexico

Coatings and thin films are used to protect against wear in many applications. If that coating also shows a low coefficient of friction, it brings better benefits, therefore, the research on coatings with these properties is of great interest. In this respect, carbon containing, or carbon-based coatings are the most popular. 52100 alloy used in wear environments has its own disadvantages. Consequently, many coating systems have been deposited on this alloy to improve its wear resistance. In this study, a multilayer coating with carbon content (WC/WCN/CNx) was deposited by High Power Impulse Magnetron Sputtering (HiPIMS) on AISI 52100 alloy. No external heating was applied during the deposition, energetic tungsten ions increase adatoms mobility that enhance adhesion. The thickness and the growth morphology of the films were studied from FE-SEM cross-sectional images. The chemical composition was analyzed by XPS. The structure of the coatings was analyzed by XRD technique. The mechanical properties (hardness and Elastic Modulus) were studied through nanoindentation techniques. The adhesion of coatings to the substrate was measured by means of scratch tests. Wear tests were performed using a tribometer with a pin on disc configuration, using a 10 mm diameter 52100 ball. The wear tracks were analyzed by SEM and the wear volume was obtained by optical profilometry. The coating showed a coefficient of friction lower than 0.3 and the wear rate was reduced 100 times relative to the substrate.

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[1] **Gaede Langmuir Award Winner**

Surface Science Division

Room 319 - Session SS+AS+SE-ThA

ALD and CVD Surface Chemistry

Moderators: Melissa Hines, Cornell University, **Dario Stacchiola**, Brookhaven National Laboratory

2:20pm **SS+AS+SE-ThA-1 ALD Surface Chemistry on Lithium-Ion Battery Cathodes*, Jeffrey Elam,*** Argonne National Laboratory **INVITED**

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) is a powerful strategy for controlling interfacial properties. ALD coatings can suppress undesirable electrochemical reactions between lithium-ion battery (LIB) cathode surfaces and the organic liquid electrolyte and improve LIB cycling stability. While numerous reports have evaluated the electrochemical performance of ALD treated cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. This presentation highlights our recent work investigating the surface chemistry of ALD on LIB cathode surfaces. We find that the nucleation and growth of Al_2O_3 ALD on$LiMn_2O_4$ (LMO) is much different compared to conventional surfaces such as hydroxylated SiO_2. For instance, LMO does not have surface hydroxyls under typical ALD conditions. During initial Al_2O_3 ALD cycles, trimethyl aluminum reacts with Mn-O bonds and reduces surface Mn ions generating C_2H_6. Al_2O_3 ALD on LMO is highly precursor-dependent and the degree of surface Mn reduction is strongly influenced by the Lewis acidity of the precursor ligands. In addition, the Al_2O_3 ALD growth per cycle (GPC) on LMO varies by 30x among 5 Al_2O_3 ALD precursors that exhibit essentially the same GPC on SiO_2. We next examined the surface chemistry for Al_2O_3 and AlF_3 ALD on 12 different cathode surfaces ranging from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC). We found that the Ni, Mn, and Co transition metals in the cathode undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, our measurements revealed the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure. This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3. ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

3:00pm **SS+AS+SE-ThA-3 Role of Temperature, Pressure and Surface Oxygen Migration in the Initial Atomic Layer Deposition of HfO_2 on Anatase TiO_2(101)***, G. D'Acunto, R. Jones,* Lund University, Sweden*; L. Pérez Ramírez,* Synchrotron Soleil, France*; P. Shayesteh, E. Kokkonen, F. Rehman,* Lund University, Sweden*; F. Lim, F. Bournel, J. Gallet,* Sorbonne Université, France*; R. Timm, **Joachim Schnadt**,* Lund University, Sweden

Atomic layer deposition (ALD) has become one of the prime methods for deposition of ultrathin films with atomic-scale precision [1,2]. Yet, for many ALD processes the underlying surface chemistry or aspects of it remain unclarified [3,4]. Experimental methods that allow the real-time monitoring of the ALD surface chemistry, i.e. time-resolved methods that can be applied during an ongoing ALD process, can provide much deepened insight into the ALD surface chemistry. One such method is time-resolved ambient pressure x-ray photoelectron spectroscopy (APXPS), which is an excellent match to ALD since it easily can be used in standard ALD pressure conditions of up to around 1 mbar. Here, we have applied APXPS to the study of the surface chemistry of the initial full cycle of HfO_2 ALD on TiO_2(101) from tetrakis(dimethylamido) hafnium (TDAMHf) and water precursors at both high (500 K) and low (300 K) surface temperature as well as high (~10^{-1} mbar) and low (~10^{-6} mbar) pressure.

Generally, we find that the initial ALD process on TiO_2(101) is characterised by an absence of surface hydroxyls, which implies that the reaction cannot proceed via the ligand-exchange mechanism standardly proposed for oxide ALD from amido complexes and water. Instead, dissociative adsorption and subsequent hydrogen insertion reactions take place during the first metal half-cycle, which lead to the formation of a number of different surface species, including a dimethyl ammonium ion and an imine. Their formation requires either a bimolecular reaction pathway or an active role of the TiO_2(101) surface as an oxygen supplier. Both pathways are viable and may compete with each other. Oxygen transport is evident from the formation of HfO_2 during the very first half-cycle and a concomitant reduction of the TiO_2 support already. The water half-cycle then allows hydroxyl formation, but only at sufficiently higher water pressure. In this case, a transition towards a ligand exchange reaction mechanism is possible, which, however, is hindered if the water pressure is too low.

Our study highlights how chemical models for transition metal oxide ALD from amido complexes and water need to be extended, by consideration of hydroxyl-free surfaces, oxygen transport and bimolecular reactions paths, and how time-resolved *in situ* studies can help understand how deposition parameters affect the growth of HfO_2.

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3:20pm **SS+AS+SE-ThA-4 ALD of Well-Defined Mixed-Oxide and Metal-Oxide Catalytic Interfaces*, Francisco Zaera,*** University of California - Riverside

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites. We will describe the development of prototypical surface sites comprised of mixtures of silica supports (mainly well-structured mesoporous materials such as SBA-15), titania thin films, and gold nanoparticles, as that combination has proven to offer some unique and useful surface chemistry for low-temperature catalysis. The materials resulting from the use of ALD approach have been characterized using a surface-science approach, relying on the use of adsorption-desorption isotherms and well-defined mesoporous structures together with electron microscopy and a variety of spectroscopic techniques, including IR, NMR, XPS, EPR, and Visible-UV absorption. They showed some unique redox properties, and were tested for the promotion of low-temperature oxidation and selective hydrogenation reactions. Time permitted, other mixed-oxide interfaces, in particular silica-alumina, will be introduced as well.

3:40pm **SS+AS+SE-ThA-5 Mechanistic studies on Catalytically Activated ALD of Fe_2O_3 on Pt*, Andreas Werbrouck,*** Stanford University, Belgium*; J. Schneider, S. Nathan, A. Rothman, S. Bent,* Stanford University

Atomic layer deposition (ALD) of Fe2O3 is well-studied process. Fe2O3 has numerous applications, for example in catalysis or as a ferroelectric material. While many Fe2O3 ALD processes have been reported, almost all of those use an iron precursor in combination with strong oxidizers such as H2O2, O3, or O2 plasma. Recently, ALD of Fe2O3 on Pt substrates has been demonstrated using just O2 gas as the co-reactant, with tert-butyl ferrocene (TBF) as the metal precursor [1]. The process was area selective, with no growth occurring on other substrate materials (SiO2, Al2O3, Au); hence, it is hypothesized that the Pt substrate creates reactive oxygen species in situ, effectively catalyzing the reaction to grow Fe2O3. Intriguingly, the activation continues after the Pt substrate has been completely covered by Fe2O3. The continued growth is attributed to the formation of a sub-surface oxygen reservoir.

In this work, we further investigate this process, with a focus on the underlying oxygen activation and transport mechanisms. In situ ellipsometry was used to study the growth characteristics and x-ray diffraction confirmed the Fe2O3 crystal structure. X-ray photoelectron spectroscopy results show a clear correlation between the amount of deposited Fe2O3 and the Pt surface coverage. To study the kinetics and mechanistic steps of the process, quadrupole mass spectrometry (QMS) was employed. H2O (m/z 18) CO (m/z 28, which is also N2) and CO2 (m/z 44) are observed as reaction products when Pt is present, indicating a combustion-like mechanism. Furthermore, as expected, the kinetics of the reservoir change as the film grows thicker; this behavior is confirmed by the QMS measurements.

Finally, a simple 1D diffusion model was developed to describe the sub-surface oxygen reservoir process (fig. 1). Given the partial pressure of O2, the model captures adsorption, transport and desorption of the oxygen in the layer before (O2) and after (O*) activation. The Pt surface coverage is parametrized too. The model yields observable outputs such as the amount of desorbing species and reaction products, but also parameters which are harder to access experimentally, such as the activation energies and kinetic constants and concentrations of the different species in the layer. Comparison of the model results with experimental data should help provide deeper insight into the mechanism of catalytically activated ALD.

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Thin Films Division
Room 316 - Session TF+AS-ThA
In-Situ Characterization of Thin Films and Interfaces

Moderators: James Fitz-Gerald, University of Virginia, **Robert Grubbs**, IMEC Belgium

2:20pm **TF+AS-ThA-1 *In situ* IRRAS and XPS for the Characterization of Gas Interactions with MOF Nanofilms***, **Tianhao Hu,*** Stony Brook University/Brookhaven National Laboratory*; C. Eads,* Max IV Laboratory, Sweden*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

The need for novel solid catalysts for use in industry has demanded the development and the application of new techniques of *in situ* spectroscopy which enables the study of catalysts in conditions close to industry. Infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) are complementary techniques that provide chemical and electronic structure information and have been widely used under *in situ* conditions. However, applying these techniques to insulating powders, such as metal-organic frameworks (MOFs), in controlled environments can be challenging. Here we grow films of archetypical MOFs, UiO-66 and UiO-66(NH_2), via a vapor-assisted conversion method and incorporate Pt catalytic sites (Pt@UiO-66(NH_2)) through solution impregnation. Using ambient pressure XPS, the electronic structure of the MOF and the oxidation state changes of the Pt are followed under various gas dosing conditions. Using infrared reflection absorption spectroscopy (IRRAS) and the adsorption of probe molecules N_2, CO, CO_2, and ethylene, under-coordinated metal sites and the acid strength of hydroxyl groups are characterized. IRRAS was also used to follow the oxidation of CO catalyzed by Pt@UiO-66(NH_2). Signature IR bands for gas phase CO_2 product and CO interacting with Pt^0 sites at 2024 cm^{-1} and 2098 cm^{-1} are found. This study highlights the information to be gained by applying traditional surface science techniques to nanoscale films for chemical, electronic, and reactivity characterization.

2:40pm **TF+AS-ThA-2 AVS Nellie Yeoh Whetten Awardee Talk: Characterizing Early-Stage Morphology and Defect Dynamics in Block Copolymer Thin Films with Environmentally Controlled High-Speed Atomic Force Microscopy***, **Julia Murphy**[1],* University of Chicago*; J. Raybin,* University of California at Berkeley*; S. Sibener,* University of Chicago

The spontaneous self-assembly of block copolymers into a variety of nanoscale morphologies makes these systems ideal candidates for next-generation lithography applications. However, industrial application requires long-range control over the domain order and orientation. Extensive work has been done to achieve linearity in nanopatterns on wafer size scales, but there is also a need to control the formation of point defects to generate, for example, T-junctions, jogs, and bends for semiconductor templating applications. As such, a fundamental understanding of block copolymer nanopattern formation and how structural defects contribute to instability in the films is crucial to achieve the perfection required to utilize these thin films as lithographic templates for nanotechnologies. Here, I present recent work on poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) thin films with environmentally controlled high-speed atomic force microscopy (AFM). By imaging films with minor variations in thickness above the glass transition temperature, we capture the early formation of hole, island, and continuous relief structures during thermal annealing. Additionally, we see how the striped nanoscale pattern develops in tandem with the changing mesoscale features. Confining the PS-*b*-PMMA in lithographic templates that are tapered in width, or wedge-shaped, generates dislocations at precise intervals locations in otherwise linearly aligned polymer domains. Examining polymer confined in these films reveals the pathways by which dislocations evolve and annihilate during thermal annealing, and how point defects in nanopatterns influence interfacial fluctuations in the surrounding polymer domains. Together, these studies contribute to the fundamental understanding of the dynamics and ordering of block copolymer thin films and reveal how topography - both native and imposed by lithography – impacts the nanoscale structure.

3:00pm **TF+AS-ThA-3 *In Situ* X-Ray Scattering Studies of the Influence of Plasma Properties on Epitaxial InN Growth by PEALD***, **Jeffrey Woodward,*** *S. Rosenberg, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Syntek Technologies*; S. Walton, S. Johnson,* U.S. Naval Research Laboratory*; Z. Robinson,* SUNY Brockport*; N. Nepal,* U.S. Naval Research Laboratory*; K. Ludwig,* Boston University*; J. Hite, C. Eddy,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) enables the epitaxial growth of ultrathin indium nitride (InN) films at significantly reduced temperatures and with atomic-level control of layer thickness. These advantages are challenged by the inherent complexity of the growth process due to the reliance on plasma surface interactions [1], which necessitates a detailed understanding of the relationship between the plasma and the growth kinetics. To this end, synchrotron hard x-ray scattering techniques are well-suited to the *in situ* study of PEALD processes, as they are capable of operating in harsh environments during chemical reactions and can provide real-time information about the structural properties of the film. One such technique, grazing incidence small-angle x-ray scattering (GISAXS), probes nanoscale fluctuations in electron density averaged across the sample, which can provide an in-depth description of surface topography [2]. Initial studies of epitaxial InN growth under fixed plasma conditions demonstrated the utility of GISAXS for understanding the kinetics of PEALD processes, and showed that the growth proceeded in a Stranski-Krastanov mode where the critical thickness for island formation and the coarsening behavior were strongly influenced by temperature [3].

In this work, we utilize *in situ* GISAXS to investigate the early-stage PEALD growth kinetics of epitaxial InN within three different plasma regimes. The GISAXS data are supported by diagnostic studies of the plasma species generation in the inductively coupled plasma source as a function of the relative concentrations of the nitrogen/argon gas mixture used in the growth process. The growth mode is found to be correlated to the production of nitrogen species in the plasma, with high concentrations of atomic N species promoting Volmer-Weber growth and low concentrations promoting Stranski-Krastanov growth. Under conditions of high atomic N production, both the island radius and critical thickness for island formation are found to increase with ion flux. Furthermore, the InN island distance and areal density are found to change only during plasma exposure, and to continue changing with exposure even after the methylindium adlayer is believed to have fully reacted with the plasma. Our results demonstrate the potential to control the growth kinetics during PEALD of epitaxial films by intentionally accessing specific regimes of plasma species generation.

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[3] J.M. Woodward *et al.*, J. Vac. Sci. Technol. A **37**, 030901 (2019)

3:20pm **TF+AS-ThA-4 Optical Monitoring of $MoCl_5$ and H_2S Delivery During Atomic Layer Deposition of MoS_2***, **Berc Kalanyan,*** National Institute of Standards and Technology*; E. Jahrman,* National Institute of Standard and Technology*; J. Maslar,* National Institute of Standards and Technology

Low-temperature (<400 °C) deposition of transition metal dichalcogenide (TMD) films has been proposed as a potential route for fabricating diffusion barrier structures in field effect transistors and other electronic devices. Atomic layer deposition (ALD) is well-suited to this application due to its low thermal budget and high conformality, enabling its integration into back-end of line processing. Several publications have described the deposition of layered MoS_2 films by ALD, most commonly using $MoCl_5$ and H_2S as precursors[1–4]. Inorganic precursors may be desirable for their high thermal stability and the lack of organic ligands, which often are a source of impurities in deposited films. However, $MoCl_5$ is a low-volatility solid under typical delivery conditions and can readily form oxychlorides upon exposure to moisture. Delivery challenges associated with $MoCl_5$ are reflected in the large variety of delivery methods and conditions reported in the literature, for instance a vessel temperature range of 70 °C to 210 °C. Deposition studies using $MoCl_5$ and H_2S also show inconsistent results with respect to MoS_2 morphology, grain size, and composition, with no deposition reported under some conditions[5]. This lack of reproducibility could stem from variations in $MoCl_5$ flux observed under different delivery configurations. To address this possibility, we monitored the flow of $MoCl_5$ and H_2S as a function of delivery conditions using direct absorbance measurements. We measured vapor phase spectra of neat $MoCl_5$ and its common oxychlorides using an ultraviolet-visible (UV-vis) spectrometer under static conditions. To evaluate precursor delivery under flow, we

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[1] **AVS Nellie Yeoh Whetten Awardee**

implemented in-line gas analyzers each consisting of a broadband source, a filter for wavelength selection, and an avalanche photodiode. We evaluated the delivery rates of $MoCl_5$ and H_2S injected from vapor draw and direct draw vessels, respectively. In addition to vapor phase measurements, we used real-time spectroscopic ellipsometry to characterize precursor adsorption under varying delivery conditions. Using results from these measurements, we will discuss the reproducibility of $MoCl_5$ and H_2S delivery rates and potential implications for MoS_2 deposition.

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3:40pm **TF+AS-ThA-5 Temperature-Time-Thickness (TTT) Topography Maps: A Parameter Space Visualization Approach for ALD Processes***, **S. Novia Berriel**, C. Feit, U. Kumar,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

In atomic layer deposition (ALD), an optimized process is characterized by its stability, predictability, and self-limiting nature. Each of these characteristics is quantified individually with separate sets of experiments. For stability, temperature is varied while holding pulse time constant. Similarly, a process's self-limiting nature is determined by saturation curves, varying the pulse time (i.e., dose) of the precursors while holding temperature constant. These data are usually presented in such as way as to imply no interdependency between them. This is a limited view of process optimization that will only yield partial understanding of deposition characteristics. We propose the information held in the interdependencies of these parameters can lead to improved process development and better control of final film properties.

We have used in situ spectroscopic ellipsometry to capture temperature-time-thickness (TTT) topography maps of ALD processes. The TTT contour plots are 3D visualization maps that demarcate dose saturation times, temperature windows, and corresponding growth rates. Based on a methodology recently published by our group[1], we demonstrate TTTs of several thermal ALD processes including CeO_2, Al_2O_3, ZnO, TiO_2, as well as plasma enhanced ALD (PEALD) of TiO_2. These topographies collectively show stability, adsorption, and reaction (i.e., thermodynamic) characteristics of the precursor reactant molecules. TTT curves are also obtained as single-substrate experiments, thus reducing process development times and resource consumption. We propose a comprehensive database of TTT diagrams can be used for improved process development and can eventually provide guidance towards the development of precursors finely tuned to the requirements of ALD processes.

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4:00pm **TF+AS-ThA-6 Surface Functionalization of Cu with Inhibitors to Enable Area-Selective Atomic Layer Deposition***, **Andrew Kaye**, S. Agarwal,* Colorado School of Mines

Area-selective atomic layer deposition (AS-ALD) is a bottom-up fabrication technique that can address challenges related to conventional lithography in the fabrication of integrated circuits. Cu is the predominant interconnect metal while SiO_2 is used as the dielectric. In this work, we explore the growth of a dielectric on SiO_2, with Cu as the nongrowth surface. Using *in situ* reflection-absorption infrared spectroscopy (RAIRS) we previously showed that thiols are effective inhibitors for Cu, and readily adsorb onto the surface by reducing the native CuO_x layer. However, thiols have a low vapor pressure and thermal stability on Cu. With these inhibitors, the Cu surface can be re-dosed between ALD cycles, which is essential in plasma-assisted ALD processes. Moreover, the inhibitor readily desorbs from the non-growth surface after AS-ALD, which eliminates surface cleaning steps that are normally required with self-assembled monolayers. Recently, several small molecule inhibitors for Cu have been reported in the AS-ALD literature including alkynes, aniline, and pyridine.

For alkynes, we show that a H_2 plasma cleaning step is required to reduce the native CuO_x layer on the Cu surface. When Cu wafers left in atmospheric conditions are exposed to an H_2 plasma, RAIRS shows that surface carbonates are removed, which indirectly confirms the presence of surface CuO_x. Specifically, we show that after we optimized the H_2 plasma cleaning duration at 200 °C, 5-decyne adsorbs on the Cu surface. The adsorption of 5-decyne is apparent from the appearance of –C=C– and –C≡C– stretching vibrations in the ~1600 and ~2200 cm^{-1} regions, respectively. In addition, we also observed the CH_x stretching and bending modes in the ~2900 and ~1400 cm^{-1} regions, respectively. Adsorption of 5-decyne on PVD and CMP Cu was observed over the temperature range of 28 to 150 °C. As the substrate temperature increased for the PVD Cu surface, the intensity of the –C=C– mode decreased while the –C≡C– mode increased, indicating that chemisorption is favored at lower temperatures while strong physisorption is favored at higher temperatures. At higher temperatures, the CH_x stretching and bending mode intensities decreased, indicating lower 5-decyne adsorption. ALD of Al_2O_3 on Cu with 5-decyne as an inhibitor was tested with dimethyl aluminum isopropoxide (DMAI) and H_2O. Even at sub saturation doses of DMAI, AS-ALD was not observed. We will also compare 5-decyne as an inhibitor with aniline and pyridine, which have been demonstrated as more promising candidates.

Applied Surface Science Division
Room Ballroom A - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP-1 Isolation of Pt Metal Atoms Using a Surface-Catalyzed Covalent Organic Framework*, David Wisman,* Indiana University Department of Chemistry; NAVSEA Crane*; Y. Bai, S. Tait,* Indiana University Department of Chemistry

Single-site metal centers in heterogeneous catalysts are highly desirable to improve reaction selectivity, due to the uniform active site geometry. It is often advantageous to have a predictable 2-D structure of single-site metal centers, making it necessary to integrate the single-site centers into an ordered array of receptor sites. One way to approach this challenge is through the formation of covalent organic frameworks (COFs). In the work reported here, we utilize a surface-assisted dehalogenation reaction of 1, 3, 5–tris(4-bromophenyl)benzene (**TBB**) to form a 2-D covalent organic framework on single-crystal metal surfaces. Following successful formation of the 2-D framework on the surface, favorable binding sites for metal catalysts (platinum) are formed by depositing 1, 10-phenathraline-5, 6-dione (**PDO**) on the surface. **PDO** becomes confined within the porous COF and is then able to stabilize vapor deposited metal and single atom sites. X-ray photoelectron spectroscopy confirms the oxidation of the platinum metal when deposited with **PDO** molecules, while scanning tunneling microscopy confirms the confinement of **PDO** within the pores, and the absence of any external 1-D Pt:**PDO** chains. The highly predictable nature of the covalent organic framework chemistry makes this an exciting result for single-site metal center formation.

AS-ThP-2 In situ Spectroscopic Evaluation of the Aging Mechanisms of Molybdenum Disulfide*, Robert Chrostowski,* University of Texas at Austin*; J. Curry, M. Dugger,* Sandia National Lab*; F. Mangolini,* University of Texas at Austin

Molybdenum disulfide (MoS2) is a lamellar transition metal dichalcogenide extensively used as a solid lubricant in the aerospace industry due to its beneficial lubricating properties (i.e., low friction) in vacuum. Unfortunately, exposure to environmental contaminants, believed to be primarily oxygen and water, degrades the tribological performance of MoS2 in a process known as "aging". While aging of MoS2 coatings has been recognized as an important engineering problem occurring even in high-vacuum, the underpinning mechanisms are still poorly understood. Developing a fundamental understanding of chemical processes occurring in MoS2 and their kinetics upon exposure to different gases can provide guidance for developing novel approaches to prevent and/or reverse aging of MoS2 coatings.

Here, we employ an in situ surface-analytical approach, based on the combined use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS), to evaluate and quantify the surface chemical changes occurring upon aging MoS2 in aerobic conditions. Additionally, in situ annealing experiments of MoS2 samples inside the XPS chamber were carried out to evaluate the effect of annealing before and after aging on the surface chemical processes occurring inside and outside wear tracks upon aging. Finally, to identify the relative contribution of oxygen and water to the aging process, MoS2 samples were exposed to deuterium oxide (D2O) and oxygen-18 (18O) in the ToF-SIMS chamber. The subsequent ToF-SIMS analyses provided evidence for the high diffusivity of water in MoS2, and, especially, in tribologically-stressed regions.

The results of these investigations, providing novel insights into the relative contribution of oxygen and water to aging of MoS2 coatings and the effect of tribologically-induced structural variations on the transport of water in the near-surface regions of MoS2, add significantly to the understanding of the mechanisms underlying the aging process.

AS-ThP-4 Stm Investigations of Self-Assembly of Proline*, Benjamin Heiner,* *A. Pittsford, S. Kandel,* University of Notre Dame

Scanning tunneling microscopy, through the observation of molecular clusters and monolayers on surfaces, provides direct experimental evidence as to how intermolecular interactions result in the self-assembly of extended structures. A detailed understanding of the interplay of interactions will result in improved understanding and prediction of the behavior of self-assembling systems, with implications in a wide range of disciplines ranging from crystal engineering to supramolecular chemistry to protein secondary and tertiary structure. We present experimental results on the self-assembly of proline, as well as the results from computational modeling. Pulse deposition of d-proline on Au(111) reveals that it forms dimer or catamer chains and pentamer clusters. The dimer structures are chiral, as would be expected from an enantiopure adsorbate; however, the pentamers on the surface appear racemically mixed. Comparison of self-assembled structures to related molecules reveals similar behavior for proline, indole-2-carboxylic acid, and indoline-2-carboxylic acid, but substantial differences are observed for pyrrole-2-carboxylic acid.

AS-ThP-5 Efforts to Improve XPS Analysis Quality in an Era of Increasingly Diverse Uses and Users*, Don Baer,* Pacific Northwest National Laboratory*; J. Watts,* University of Surrey, U.K.*; A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico*; M. Linford, G. Major,* Brigham Young University

Use of XPS in publications continues to increase exponentially but anecdotal reports and systematic analyses show a growing presence of significantly flawed data and analyses. Examination of six months of XPS data in three journals found more than a quarter of the data presented to be highly flawed, often leading to incorrect conclusions. Recognition of this problem within the surface analysis community has increased with recognition that inexperienced users and increased use of XPS outside the surface analysis community contribute to the problem. Several efforts have been initiated to address the problem. This poster will identify some of the specific problems and describe some of the community efforts intended to address them. Challenges associated with reliable repeatable XPS measurements were recognized at the advent of commercial instrumentation and led to the formation of relevant ASTM and ISO standards committees. Recent efforts to address problems found in the literature include, review papers and tutorials including collection of papers on reproducibility with a focus on XPS in the Journal of Vacuum Science and Technology A (JVSTA), websites containing and summarizing useful information, implementation of expert systems to assist the collection and analysis, advanced software tools, and online forums that can enable community interactions to assist analysts. The poster focuses on evolving efforts to address three specific issues: i) incomplete data and analysis reporting, ii) the need for bite sized versions of important information for non-experts and iii) the high rate of peak fitting problems. Examination of XPS containing papers finds that information important for reproducible XPS results is often very incomplete. Approaches to develop, distribute, and encourage use of essential analysis information are being explored. To address the shorter attention spans of many in the age of online media and social networks papers to provide incremental bites of useful information are being developed for a series of paper to appear *Surface and Interface Analysis*. Multiple efforts are underway to address the high rate of problems associated with photoelectron peak fitting. These include guides to peak fitting, guides to peak identification and fitting for specific elements, and development of a peak fitting social network designed to connect new and experienced XPS users. In addition, development of a second JVSTA collection of Reproducibility Challenges and Solutions papers is under way.

AS-ThP-6 Metrology Developments in XPS and HAXPES*, David Cant,* *B. Reed, A. Shard,* National Physical Laboratory, UK

X-ray photoelectron spectroscopy (XPS) is a highly quantitative and surface sensitive technique for analysis of the chemical composition of a given sample. However, it is important that the data obtained during a photoemission experiment is interpreted correctly – both instrumental and sample-related factors must be accounted for to obtain a quantitative understanding of the sample composition. It is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument, as well as the *sample-dependent relative sensitivity factors* (RSFs) which account for the differences in emitted electron intensities for each peak.

In a recent VAMAS interlaboratory study, the huge variability of transmission functions between different laboratories and instruments has been demonstrated, underlining the need for an ISO standard on XPS intensity calibration which is now being developed under the auspices of ISO TC201 "Surface Chemical Analysis". Here we present instrument geometry-corrected reference spectra of low-density polyethylene (LDPE) for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Sensitivity factors are required to account for differences in the intensity of emitted electrons from different materials within a sample. Such differences arise due to several factors, including the photoionisation cross-section; electron kinetic-energy-dependent variations in transport through a material; and the anisotropic emission of excited electrons. Theoretically determined sensitivity factors, such as the NPL AMRSFs for Al and Mg anode instruments,are commonly used.

For hard x-ray photoelectron spectroscopy (HAXPES), photoionisation cross-sections decrease significantly as photon energy increases, and anisotropy effects become more complex due to the increased contribution of non-dipolar effects. It is therefore increasingly important that a careful consideration be given to the estimation of RSFs. This is further complicated by the multiple photon energies and instrument geometries available in commercially available HAXPES instrumentation. Here we present a set of formulae, derived from fitting of theoretical database values, which allow the estimation of AMRSFs for instruments using any photon energy in the range 1.5 keV - 10 keV, with any instrument geometry. A few instrument geometries in which X-rays are polarised are insensitive to angular emission effects, and these are highlighted in this work.

AS-ThP-7 Advances in Automated XPS Analysis – from Data to Answers*, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc*; K. Good, K. Macak,* ***Christopher Blomfield,*** Kratos Analytical Limited, UK

XPS has become a mainstay of the suite of analytical tools available for characterisation of new materials and processes.It would be fair to say that XPS instrumentation is now viewed as a “tool” by many users and the expectation is therefore that results are automatically produced.Here we discuss the latest improvements and advancements which provide not just data but results and answers.We look at improving peak identification from unknown samples and automatic region spectral acquisitions.In addition, we show how known samples can be quickly and efficiently acquired and processed to provide comparison results for QA or trend analysis.

AS-ThP-10 The Role of Artificial Intelligence in Minimizing Analysis Errors, Illustrated with EXAFS, Nanoindentation, and Core Level Photoemission*,* ***Jeff Terry,*** Illinois Institute of Technology

We have developed artificial intelligence based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS) measurements. This development will help to address the reproducibility problems that slow research progress and inhibit effective tech transfer and manufacturing innovation in these scientific disciplines. A machine learning approach was applied to the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy measurements collected using a synchrotron radiation facility. Specifically, a genetic algorithm was developed for fitting of the measured spectra to extract the relevant structural parameters. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. It requires the use of Larch and Feff for calculating the initial EXAFS paths. We have recently extended the code to make use of Feff8.5lite so it can calculate the paths needed for populating the analysis from within the EXAFS Neo package. The code base has been expanded for the analysis of nanoindentation data and simple x-ray photoelectron spectroscopy measurements. The publication describing the analysis package and where to obtain the software can be downloaded at: https://doi.org/10.1016/j.apsusc.2021.149059 or by contacting the speaker.

AS-ThP-11 X-ray Photoelectron Spectroscopy of Polymer Electrolyte Membrane Fuel Cell Components*,* ***Maxim Shepherd,*** *S. Pylypenko,* Colorado School of Mines

Development of sustainable technologies that produce energy are extremely important to reduce the environmental impacts of current technologies. Proton exchange membrane fuel cells (PEMFCs) generate clean energy using hydrogen and oxygen with water as the main byproduct. The state-of-the-art catalyst for the oxygen reduction reaction occurring at the cathode is based on Pt nanoparticles dispersed on carbon support (Pt/Carbon). The cathode catalyst layer has a major influence on the overall cost of a PEMFC due to the loading of platinum that is needed to achieve a reasonable power density. Optimization of the catalyst layers to achieve the most efficient distribution of the ionomer coating which directly effects the mass transport and device efficiency, is one of the current needs especially for catalysts layers produced using scalable routes. Furthermore, there is a general lack of understanding about how the catalyst support, catalyst, and ionomer interact with one another on a molecular scale. This work utilizes X-ray Photoelectron Spectroscopy (XPS), a highly surface sensitive technique to characterize elemental and chemical speciation of the catalyst layers. XPS is a very common technique to study catalyst but has not been widely applied to investigate catalyst layers.This poster will provide a general background on sample preparation, and data acquisition and analysis of catalysts and catalysts layers made with platinum on High Surface Area Carbon (HSC) catalyst, including findings related to Nafion ionomer degradation. Furthermore, this poster will present comparison of chemistry of the catalyst before and after incorporation into catalyst layer, and will discuss composition of catalyst layers as a function of ionomer loading.

AS-ThP-12 Nanoscale Surface Sensitive Chemical Imaging of Additive Manufacturing Materials*,* ***Ashley Maloney,*** *K. Artyushkova,* Physical Electronics USA*; O. Renault, E. De Vito,* CEA/LETI-University Grenoble Alpes, France

Additive manufacturing is an ever-growing area of research interest that depends upon the high quality of precursor materials in order to achieve a robust final printed product. In this work, an alloy powder material of CuCrZr used in the laser-powder bed diffusion process of 3D printing will be analyzed for grain boundary diffusion and for chemical variation among different particle sizes. Recent advances in Auger Electron Spectroscopy, including *in situ* FIB capabilities, put AES at the forefront of surface analysis techniques with respect to characterization of such defects on the nanoscale. The quantitative elemental information AES provides from solid surfaces combined with FIB tomography allows for *in situ* cross-sectioning and subsequent elemental characterization of the CuCrZr powder particles. The variation of chemistry across different sized particles will also be assessed via quantitative chemical analysis using XPS.

In this work, CuCrZr alloy powder particles were cross-sectioned and analyzed using a PHI 710 scanning Auger nanoprobe equipped with a 25kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). We demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site-specific imaging of grain boundary diffusion within the alloy.

AS-ThP-13 Data Reporting in XPS: A Consistent Lack of Information*,* ***Max Clark,*** *G. Major, M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is widely used to probe the top 10 nm of materials. It is based on the photoelectric effect. Spectra acquired in XPS typically require peak fitting. To properly peak fit, various mathematical functions, including the background and peak shapes, are used. Additionally, different experimental conditions typically change the types of peaks that are required for a fit. We have surveyed the XPS reporting from 2021 papers in three major journals. About 900 papers were surveyed. Only 70% listed the XPS instrument that was used. Among publications with fitted XPS data, over 90% did not indicate the line shape(s) used and over 35% did not indicate the background used. In this presentation, we provide information on other aspects of reporting as well. To improve the reporting in the literature, which should improve the reproducibility of studies, we recommend that (at a minimum) the following be reported:

1. The manufacturer and model number of the photoelectron spectrometer
2. The X-ray anode and energy (for example, in conventional XPS, Mg K⍰ or Al K⍰ with energies of 1253.6 or 1486.6 eV, respectively)
3. The type of source: non-monochromatic or monochromatized
4. The X-ray power and spot size
5. The photon energy used in the measurement, along with energy resolution
6. The vacuum level during the analysis Additionally, information about the line shape(s), fitting program, peak positions, and background should also be included if fitting data.

AS-ThP-14 Electrochemical Flow Cell for Surface and Interface Analysis Cluster*, **Soniya Gahlawat,*** CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria*; M. Valtiner,* TU Wien/IAP, CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria

Electrochemistry plays a pivotal role in scientific and technological advancements. In order to achieve the circular carbon neutral economy goals, we need to advance our infrastructure to study electrochemical processes such as hydrogen production, batteries, fuel cells, recycling, and corrosion. The common feature in all these processes are interface reactions and the key to further development is improving the understanding of these phenomena.

In fundamental research, we have seen increasing use of classical Ultra-High Vacuum (UHV) analysis techniques at higher pressures, although the pressure range is still well below atmospheric conditions and even more so below operating conditions of any real-world electrochemical device.[1] Therefore, we decided to mimic the real operating conditions for electrochemical devices and combined with UHV surface and interface analysis techniques. We integrate the electrochemistry into a UHV system for quasi-operando analysis to explore the energy storage and conversion research areas at nanoscale.

The major challenge with operando and in-situ clusters is to have an ideal electrochemical flow cell suitable for studying the solid/liquid interface dynamics. Most of the cells with easy transfer of working electrode have poor electrode geometries, which results in high ohmic resistance. Additionally, it is pertinent to prevent the presence of organic impurities in the cell as they may get adsorb at the surface and obstruct the surface-interface analysis. We have initiated the development of our experimental setup based on a cell designed by Olaf Brummel[2] and tried to overcome the above-mentioned limitations. To avoid the glass corrosion, the lower part of cell is designed with Teflon and further the geometry of the cell is modified in a unique way. I will present my initial results in this direction as well as an overview of electrochemical surface and interface analysis cluster being developed at TU Wien.

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AS-ThP-15 Optical Measurements of Temperature Driven Phase Change in Doped Niobium Oxides for Neuromorphic Computing Applications*, **James Michels**, Z. Robinson, V. Daviero,* State University of New York College at Brockport*; K. Beckmann, N. Cady,* SUNY Polytechnic Institute, Albany

Significant research has focused on low-power stochastic devices built from memristive materials. These devices foster ‘neuromorphic’ approaches to computational efficiency enhancement in merged biomimetic and CMOS architectures. Niobium dioxide has volatile memristive properties that include a phase change from an insulating to a conductive state at temperatures above around 800C. This phase change makes it an ideal candidate for future neuromorphic electronics. An ultra-high vacuum technique for measuring the effect of dopants on the phase change has been built, and relies on *in situ* infrared spectroscopy to assess the effect of the phase change on optical reflection and transmission. Further, changes in the macroscopic optical absorption properties of titanium doped NbO_2 are presented as a function of temperature and optical wavelength. The results reveal an interesting optical transmission behavior in a localized temperature range in contrast to its overall decrease with increasing temperature. The latter may provide modulation capabilities for memristive devices.

AS-ThP-16 Laser Surface Melting to Mitigate Intergranular Corrosion of Sensitized AA 5083*, **Md Sojib Hossain,*** University of Virginia, USA, Bangladesh*; J. Skelton,* University of Virginia*; W. Moffat, A. Wang, G. Lu, J. Fitz-Gerald,* University of Virginia, USA

The precipitation of an anodic Mg-rich phase in 5xxx series aluminum alloys causes them to become sensitized and highly susceptible to corrosion, especially when used in marine-based applications. Heat treatments (>240°C) can dissolve the secondary phases back into the matrix but are unrealistic for service components. In this study, laser surface melting (LSM) is used to reverse the sensitization at the alloy’s surface. An excimer ns-pulsed laser was employed at a fluence of 1.5 J/cm 2 to rapidly melt and solidify the surface of highly sensitized AA5083 samples. Characterization of the composition, roughness, and corrosion resistance of these samples were performed to achieve a holistic understanding of how the alloy surface changes after laser melting. Results show that laser processing decreased the open circuit potential from -780 mV to -980 mV (vs. SCE) due to surface homogenization and dissolution of secondary phases, which contribute to micro-galvanic corrosion. A reduction in the corrosion rate was attributed to the dissolution of anodic precipitates into the solid aluminum solution within the melted region, approximately 7 um deep beneath the surface. This work illustrates the efficacy of using LSM to reverse the sensitization of Al-Mg alloys, leading the way toward a method of restoring the original corrosion resistance of sensitized in-service material

AS-ThP-17 Chemistry and Mechanism of Two-Dimensional Transition Metal Carbide and Nitride Mxene Synthesis*, **Mark Anayee**, R. Wang, Y. Gogotsi,* Drexel University

MXenes comprise a family of two-dimensional carbides and nitrides that has grown to encompass numerous structures and compositions – >30 single transition metal MXenes with a near infinite number of solid solutions ranging in thickness depending on the number of atomic layers, from 5-11. MXenes are promising for a variety of applications ranging from electrodes for energy storage to wireless communication, optoelectronics, and medicine because of their high electrical conductivity, redox-active surfaces, plasmonic behavior, and other attractive properties. MXenes are typically derived *via* topochemical etching of atomically thick layers from precursor layered MAX phases using corrosive halogenated aqueous or vapor etchants. Knowledge of the reaction mechanism and process kinetics are of fundamental importance for the synthesis and property control of MXenes. Prediction of the optimal synthesis approaches will facilitate new MXene composition discovery and prediction of optimal processing time as a function of various parameters will also facilitate scaling up the wet chemical synthesis of MXenes for industrial use. Despite their importance, such studies have been challenging because of the atomic thickness of the A-element layers being etched and the aggressive etchants that hinder in situ studies. Herein, we investigate the defects in the metal and carbon site in the parent MAX phase using ex situ photoemission spectroscopy and mass spectrometry to understand how MXenes develop from MAX phases. Moreover, we investigate the effect of such defects and MAX structure and chemistry influence the etching reaction mechanism through in situ optical profilometry and Raman spectroscopy of single MAX particles to monitor the structural and chemical transformation. Through these methods, we gain fundamental understandings of atomic etching mechanism and kinetics for layered materials and how the reaction starts, proceeds, and finishes.

AS-ThP-19 Multilayer Method Modification for the Quantitative Chemical Composition Analysis on Initial Oxidation of Nickel*, D. Guzmán Bucio, G. Gómez Sosa, D. Cabrera German , M. Bravo Sánchez, J. Torres Ochoa, O. Cortazar Martínez , A. Carmona Carmona, **Alberto Herrera Gómez**, M. Mayorga-Garay,* CINVESTAV-Unidad Queretaro, Mexico

Peak-fitting of the Ni 2p core-level from metallic nickel and its oxides is challenging due to the high asymmetry of the main peak, the complex multiplet structure, and the intense Shirley-type background. This work presents X-ray photoelectron spectra acquired from a clean metallic Ni film (sublimated on Si [001]). These are analyzed with two approaches that account for the apparent asymmetry of the main photoemission line: one being the use of the double Lorentzian asymmetric line shape; the other, a set of symmetric peaks. Both approaches lead to excellent fits with undistinguishable peak envelopes and backgrounds; however, they lead to different sets of previously unreported low-intensity satellites. The application of the Block Approach to the analysis of the partially oxidized Ni spectra allowed for the robust identification of five doublets corresponding to the oxide. It is remarkable that the sum of these oxide peaks closely reproduces the Ni^{3+} spectra, which is consistent with the assessed composition ($Ni_2O_{3.1\pm0.3}$). The strong overlap and shape similarity of the Ni0 $L_3M_{45}M_{45}$ Auger structure with that of the Ni^{3+} strongly suggests that the Auger Parameter modified does not provide additional information to that provided by the binding energy shift of the 2p core level. The latter is in contrast to the claims made by other specialists. The angular dependence of the peak intensities is not consistent with a simple layer oxidation mechanism but with the formation of oxide regions protruding deeper into the film. The existence of regions with protrusions might depend on the grain orientation. For the first time in the history of X-Ray Photoelectron Spectroscopy, in the analysis of the surface chemical composition and the morphology, the uncertainty propagation methods were applied considering the covariance between the parameters of the depth profile parameters and those of the chemical composition.

2D Materials Technical Group
Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, **Jyoti Katoch**, Carnegie Mellon University

8:20am **2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene***, A. Ebrahimi, **Derrick Butler**, V. Kammarchedu, K. Zhou,* Penn State University **INVITED**

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates.Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

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9:00am **2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications***, **Minsu Oh**, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde,* Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 µm, which targets 773K blackbody temperature, with a bandwidth of less than 1.5µm. The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am **2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution***, **Fei Yao**,* University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2. On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, *etc.*), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched MoS_2/MXene/CNT composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency (7 s^{-1} at - 0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D MoS_2/MXene integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2, conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am **2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors***, **Keun Su Kim**,* Yonsei University, Republic of Korea **INVITED**

The tunable band structure of two-dimensional quantum mater is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

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10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions***, **Ayelet Vilan,*** Weizmann Institute of Science, Israel*; N. Kumar Gupta,* National University of Singapore*; S. Kumar Karuppannan,* National Quantum Fabless Foundry, Singapore*; R. Reddy Pasula,* Nanyang Technological University Singapore*; J. Martin, W. Xu,* National University of Singapore*; E. May,* Nanyang Technological University, Singapore*; A. Pike,* Newcastle University, UK*; H. Astier, T. Salim,* National University of Singapore*; S. Lim,* Nanyang Technological University, Singapore*; C. Nijhuis,* University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (AfFtn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level ("Dirac point"), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS$_x$ Electrocatalysts***, **Lee Kendall,** G. Zangari , S. Mc,* University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage.To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations.MoS$_2$ has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS$_2$ is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G^{H}_{0,ads-}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H_2 evolution, the catalytic performance of MoS$_2$ is still far from the needed requirements. To address this, researchers have investigated amorphous MoS$_x$ due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS$_x$ is an attractive candidate for electrochemical processes.This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active.To increase their activity, we investigated incorporating selenium into MoS$_x$ due to the success in crystalline, selenium alloyed MoS$_2$. This success centered on obtaining a more thermoneutral ΔG^{H}_{ads} for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively.To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS$_x$ polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS$_x$ and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS$_x$ thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics***, **Dmitry Kireev,** D. Akinwande,* The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum diselenide (PtSe$_2$) and platinum ditelluride (PtTe$_2$) to construct the thinnest elements of skintronics - electronic tattoos. The PtSe$_2$ and PtTe$_2$ e-tattoos that can be grown at comparably low temperatures (400ºC) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made insusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response***, J. Jaiswal ,* Indian Institute of Technology (Banaras Hindu University) , India*; **Marshal Dhayal,*** Indian Institute of Technology (Banaras Hindu University) , India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

Radiation Effects on Materials Focus Topic
Room 318 - Session RE+AS-FrM

Materials Analysis and Characterization with Radiation

Moderators: Scott Dubowsky, University of Illinois at Urbana-Champaign, **Camilo Jaramillo-Correa**, Pennsylvania State University

8:20am **RE+AS-FrM-1 Characterization of Materials and Surfaces with Various Types of Radiation***, **Zachary Robinson,*** SUNY Brockport **INVITED**

In this talk, I will present an overview of various types of radiation that surface scientists use to characterize materials. In particular, I will focus on my recent work studying materials relevant for post-CMOS neuromorphic computational devices. These materials provide a potential path towards improved power and computational efficiency in a merged biomimetic and CMOS architecture. For this project, we characterized niobium oxides (NbO_2 and Nb_2O_5) using photons ranging from the infrared and visible for quantitative microscopy and spectroscopy through X-rays generated both at synchrotron sources and in benchtop instruments for diffraction and photoelectron spectroscopy. In particular, broad spectrum radiation allows us to study changes in composition and structure brought about in the as-deposited amorphous thin films upon annealing. The various sources of radiation inform our understanding of the material properties by providing information about the crystal structure, stoichiometry, impurities, crystallization percentage, and optical properties. Since undergraduate students were also an integral part of this work, I will describe our efforts in finding ways for them to be productive over a short (8-10 week) summer research internship when using relatively complicated instrumentation.

9:00am **RE+AS-FrM-3 High-Energy (MeV), Heavy Ion Irradiation of Chalcogenide Phase Change Thin Films*, David Adams*, *E. Lang, T. Clark, C. Sobczak, E. Scott, J. Custer,* Sandia National Labs*; T. Beechem,* Purdue University*; K. Hattar, M. Kalaswad, M. Rodriguez,* Sandia National Labs

Phase change thin films continue to attract interest for applications such as non-volatile electronic memory, sensors, and nanophotonics, because the material can be rapidly switched between amorphous and crystalline states accompanied by large changes in electronic and optical properties. In particular, the germanium-antimony-tellurium system remains a benchmark for studies wherein $Ge_2Sb_2Te_5$ has received much attention. In this study, we have evaluated the response of various chalcogenide thin films to high energy, heavy ion irradiation in order to provide additional insight into phase stability. Crystalline $Ge_2Sb_2Te_5$ and $(Ge_2Sb_2Te_5)_xC_{1-x}$ thin films were irradiated with 2.8 MeV Au ions to different doses and characterized subsequently using Raman spectroscopy, X-ray diffraction, thermoreflectance, Transmission Electron Microscopy and 4-point probe methods. Irradiation experiments were specifically designed to induce disorder while avoiding substantial incorporation of projectile species into films therein preserving the as-deposited film chemistry. Specifically, the 2.8 MeV energy was chosen so that ion range > film thickness which leads to less than 0.01 mol.% of projectile species residing within 100 nm-thick chalcogenide films, according to SRIM estimates. Irradiation led to significant changes in both structure and properties. Pure $Ge_2Sb_2Te_5$ thin films were amorphized when irradiated above a threshold dose, ~1e12 cm^{-2}. Both the thermodynamically-stable trigonal and metastable cubic phases were disordered with concomitant changes in electrical resistivity and thermal conductivity observed. Various $(Ge_2Sb_2Te_5)_xC_{1-x}$ $[0 < 1-x < 0.12]$ thin films were also amorphized when irradiated above threshold doses. As with pure $Ge_2Sb_2Te_5$, structural disordering was accompanied by increased electrical resistivity and decreased thermal conductivity. Further insight into collisional-induced disordering was revealed by In-situ Ion Irradiation Transmission Electron Microscopy (I^3TEM). In-situ transmission electron microscopy and electron diffraction mapped the phase-specific response of films confirming different threshold doses for cubic and trigonal phases. Additionally, I^3TEM has been used to study the effects of increasing carbon concentration on phase stability and ion radiation response.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

9:20am **RE+AS-FrM-4 Multiwavelength Raman Microscopy Used to Characterize Surfaces for Plasma-Wall Interaction Study in Tokamaks*, Cedric Pardanaud*,** *C. Martin, P. Roubin,* Aix-Marseille University / CNRS, France **INVITED**

Tokamaks aim to study the possibility to produce energy by exploiting hydrogen isotope nuclear reactions. The fusion plasma is confined magnetically, but a cold plasma is in interaction with the inner walls. This plasma-wall interaction, heterogeneous at the scale of the machine can lead to component melting, surface erosion, element migration inside the chamber, dust production, tritium retention, impurity contamination, mixed material formation… These walls were made of carbon in previous tokamaks (abandoned due to formation of thick hydrogenated rich deposits). Inner walls are now composed of tungsten and/or beryllium, presenting good thermal and chemical properties.

I will demonstrate that multiwavelength Raman microscopy is a suitable technique for *post mortem* analyses of tokamak plasma facing components [1]. It delivers an information related to chemistry, which is complementary to the classically used Thermal Desorption Spectroscopy (TDS) and Ion Beam Analyses (IBA). I will focus on analyses of both laboratory made samples and samples collected inside some tokamaks.

I will illustrate my talk by presenting first how Raman, IBA and TDS of amorphous carbon deposits found inside the Tore Supra tokamak compare [2, 3]. Then, I will focus on the defective beryllium system in the JET tokamak [4- 6] and formation of beryllium hydrides [7]. I will finish by presenting some results about tungsten oxides [8, 9].

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Nuclear fusion 60 (2020) 086004

10:00am **RE+AS-FrM-6 In Situ Optical Characterization of High Temperature Defect Kinetics in Mixed-Conducting Oxide Films*, Nicola Perry,*** University of Illinois, Urbana-Champaign **INVITED**

Thin films represent model platforms for the evaluation of new materials for intermediate-to-high temperature electrochemical devices, including electrolyzers and fuel cells. We focus on candidate perovskite-structured mixed- or triple-conducting electrode materials where the bulk mobile ions are oxide ions or protons, and the surface reactions of interest are oxygen reduction/evolution, hydration, and combinations of the two in the form of hydrogenation. Central to their performance is the dynamic defect behavior at temperatures from 300 – 700 °C, particularly the kinetics of defect transport (diffusivities, *D*) and interfacial reactions (surface exchange coefficients, *k*). Conventionally, electrochemical or electrical methods that place precious metal current collectors on the electrode surface are applied to evaluate the ion fluxes; however, we have demonstrated that the presence of such metals actually alters the measured parameters (e.g., *k*) aiming to quantify surface defect kinetics and bulk defect equilibria. Instead, we exploit the coupling between defect concentrations and UV-vis optical absorption to provide contact-free, continuous, and *in situ* evaluation of the films' defect kinetics via isothermal optical transmission relaxation (OTR) responses to step changes in gas-phase chemical potentials. This method has enabled us to observe the evolution of oxygen exchange kinetics during crystallization, where the onset of crystallization corresponds to the initiation of "breathing" by the films, and we demonstrate orders-of-magnitude enhancements in oxygen surface exchange kinetics in films grown by the low-temperature crystallization method vs. conventional high-temperature-grown films. We also have developed a two-dimensional OTR technique to observe defect kinetics across all regions of 1 x 1 cm^2 films simultaneously, of use in cases with spatially heterogeneous responses. We applied this 2D-OTR to model metal | perovskite heterointerfaces to further underline the catalytic effect of metal current collectors on mixed conductors for oxygen exchange and show the surprisingly large spatial extent of that effect away from the interface. Most recently we demonstrated the ability of the OTR method to evaluate hydrogenation kinetics in proton-conducting thin films for the first time, enabling quantitative comparison of candidate new triple-conductor electrodes. Origins and applications of the optical absorption-defect concentration relationship will be discussed.

Funding Source: DOE BES Grant # DE-SC-0018963

10:40am **RE+AS-FrM-8 Exploring the Effects of Radiation on Planetary Surfaces through the Analysis of Experimental Analogs and Returned Samples from the Moon and Asteroids*, Michelle Thompson,*** Purdue University **INVITED**

Materials on the surfaces of airless bodies are continually exposed to the harsh environment of interplanetary space through a process known as space weathering. Space weathering alters the microstructure, chemistry, and optical properties of grains on the surfaces of bodies like the Moon and asteroids. This process is driven by two primary mechanisms: hypervelocity dust impacts, and the interaction of surface material with energetic particles from the solar wind. We can investigate the effects of these processes by performing laboratory experiments and by analyzing materials collected by sample return missions. Samples returned from the Moon via the Apollo missions and from near-Earth asteroids Itokawa and Ryugu by the Hayabusa and Hayabusa2 missions, respectively, have demonstrated that the microstructural and chemical characteristics resulting from solar wind irradiation are complex. Solar wind ions work to vesiculate and amorphize the outer rims (<100 nm) of grains on the surfaces of these bodies, and the depth and degree of this amorphization (e.g., presence and distribution of nanocrystalline domains) varies significantly in relation to the grain composition and its exposure timescale to interplanetary space. Similarly, solar wind radiation can cause preferential sputtering and redeposition, radiation-enhanced diffusion, and/or recoil mixing which can develop atomic-scale chemical heterogeneities on grain rims. We observe such multilayer rims with segregated cation/anion structures in solar wind irradiated silicate minerals from both the Moon and asteroids. In addition, high-energy Fe-group nuclei from solar flares create trails of ionization damage called solar flare tracks. The concentration of these tracks can be used as a proxy for the exposure timescale a grain has experienced on an airless planetary surface. We can further understand these microstructural and chemical characteristics by conducting experiments in the laboratory using ions and energies appropriate for the solar wind. This work has revealed fundamental discrepancies between experimental and natural space weathering, including the rate at which samples amorphize and the development of vesiculated textures. Such results suggest that ion flux, grain composition, and microstructure play a significant role in the development of atomic-scale irradiation characteristics in returned samples. A combined approach of sample analysis and experiments enables us to investigate how solar wind irradiation alters materials throughout the solar system which is critical for building an understanding of the evolution of planetary surfaces through time.

11:20am **RE+AS-FrM-10 Ground-Based Space Environmental Testing of Materials and Components for Spacecraft Mission Assurance***, **Sven Bilén**, J. McTernan, C. Zawaski,* The Pennsylvania State University **INVITED**

Space presents an extreme environment for spacecraft materials and systems. For example, in the low-Earth-orbit (LEO) space environment, materials and structures are exposed to high vacuum (10^{-4}–10^{-5} Pa), thermal cycling (−150 to 150 °C), ultraviolet light (100–200 nm), space radiation, potential surface impact from micrometeorites and orbital debris (MM/OD), and atomic oxygen (AO). Materials showing promise for future use in space must be assessed and evaluated for their reaction to exposure to the space environment before being baselined for inclusion into critical space infrastructure. Such evaluation can occur via *in-situ* experiments on space vehicles, but such testing is costly, of limited throughput, experiences significant time lags, and provides less specific information to identify points of failure. Ground-based testing of materials and systems under simulated space environmental conditions can address these limitations. Indeed, space hardware, depending on mission assurance requirements, goes through a battery of testing in space-simulation facilities, such as thermal–vacuum, vibration, acoustic, EMI, etc.

Penn State has facilities for full-scale testing of small spacecraft (e.g., 3-U CubeSats) in a LEO–type environment, individual components and materials, spacecraft charging mitigation schemes, and spacecraft–plasma interactions. This facility is comprised of a vacuum chamber capable of thermal cycling through a range of realistic temperatures, a plasma source capable of producing streaming ions (1–4 eV) and low-energy electrons (~0.1 eV), shake tables, anechoic chambers (for EMI testing), outgassing assessment, and radiation (via its Radiation Science and Engineering Center and Breazeale Reactor). This facility is also capable of testing individual components, whose operation is dependent on the plasma environment (e.g., thermionic cathodes, field emitters, plasma diagnostic tools, *in-situ* diagnostics such as Langmuir probes, etc.). System-wide tests that combine multiple tests are beneficial as results can be interdependent. For example, thermal cycling under vacuum that causes outgassing could contaminate sensors or other diagnostic tools such as Langmuir probes. We are working to add atomic-oxygen exposure, increased thermal range, high-energy electron exposure, UV exposure, and simulated MM/OD damage (via short, focused laser pulses) to our capabilities.

Surface Science Division
Room 319 - Session SS1+AS+HC-FrM
Oxide Surface Structure and Reactivity

Moderators: Andrew Gellman, Carnegie Mellon University, **Zhenrong Zhang**, Baylor University

8:20am **SS1+AS+HC-FrM-1 Operando Photoluminescence Microscopy Study of Photoreduction of Resazurin on Tio$_2$ Microcrystals***, **Hao Zhu**, Z. Zhang, W. Lu, B. Birmingham,* Baylor University

Titanium dioxide (TiO_2) has been extensively studied for its photo-reactivity-related applications in solar cells, clean hydrogen energy, and environmental remediation. It is commonly accepted that the anatase (A) phase is more photoreactive than the rutile (R) phase. However, the reversed relative photo activities were often reported. In addition, mixed-phase TiO_2 has shown the highest photoactivity but the synergetic effect is not clear. Understanding the syngenetic effect at the two-phase interface will lead to a new era of catalyst design.

In this work, operando photoluminescence microscopy was used to investigate the photoreduction of resazurin on anatase microcrystals, rutile microcrystals, rutile (110) single crystals, and anatase (001) single crystals. Our results show that the rate of resazurin photoreduction on the rutile (110) surface was higher than that on the anatase (001) surface. The reaction rates on anatase microcrystals with a large percentage (001) facet are faster than that on anatase (001) single crystals and close to the reaction rate on rutile (110) single crystals. The reaction rate of the anatase microcrystals depends on the morphology and structure of each individual particle. The mechanism of the syngenetic effects at the rutile/anatase interface was also studied on the synthesized A-R two-phase microcrystals.

8:40am **SS1+AS+HC-FrM-2 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO_2 Hydrogenation***, **Si Woo Lee**, M. Lopez Luna, S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing intermetallic compounds and alloys with transition metals have recently been reported to be active in the hydrogenation of CO_2 to methanol. However, the promotional role of Ga in these catalysts is still poorly understood, in particular due to the lack of information about the *surface* structures of the catalysts, especially under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted TM catalysts.

In this work, we employed *in situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make possible the studies of surfaces in the reaction atmosphere, to monitor the structural and chemical evolution of the Ga/Cu surfaces in the CO_2 hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered c(2×2)-Ga/Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface. Thus, NAP-STM studies revealed that the surface undergoes de-alloying and phase separation into Ga-oxide and (1×1)-Cu exposing Ga-oxide/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image on Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer with $(4\sqrt{3}\times4\sqrt{3})R30^\circ$ superstructure when grown on Cu(111). From NAP-XPS studies on Ga/Cu(111) in the presence of CO_2 and H_2, the formation of formate was observed, and this intermediate was finally transformed into methoxy at elevated reaction temperatures, the final surface-bound intermediate of methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that the further reaction does not occur any more from chemisorbed $CO_2^{\delta-}$ on Cu alone. Therefore, the GaO_x/Cu interface formed under reaction conditions may expose catalytically active sites, that should be taken into account for elucidating the reaction mechanism on the Ga-promoted systems. For the first time, our *operando* surface characterizations reveal strong evidence that Cu–Ga catalysts are activated in CO_2 hydrogenation with the formation of embedded oxide-metal interfacial sites by de-alloying transition, which allow us to prove the promotional role of Ga in Cu-Ga catalysts.

9:00am **SS1+AS+HC-FrM-3 Stabilization of Active Cu Sites on Oxide Surfaces***, **Dario Stacchiola**,* Brookhaven National Laboratory **INVITED**

Cu-based catalysts are active for partial and full oxidation reactions. Copper can be oxidized under moderate oxidant pressures and temperature to Cu_2O, and further to CuO under typical catalytic reaction conditions. We present here model systems using both copper oxide thin films and single crystals used to interrogate the effect of alkali, metal, and oxide modifiers on the stability of exposed active Cu sites. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

9:40am **SS1+AS+HC-FrM-5 An optimized IRAS Setup to Investigate Adsorbates on Metal-Oxide Single Crystals***, **David Rath**, J. Pavelec, U. Diebold, M. Schmid, G. Parkinson,* TU Wien, Austria

The IRAS system GRISU (**GR**azing incident **I**nfrared absorption **S**pectroscopy **U**nit) was developed to investigate adsorbates on metal oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with a UHV chamber [1].

The compact design utilizes only one CF150 flange (6") on the UHV chamber, ensuring the precise positioning of all the optical components and the high-performance requirements.

The system features five mirrors for beam guidance placed in HV and UHV environments and optimizes the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorized optical components, and apertures that control the shape of the illumination area on the sample to reduce the background signal. A second aperture limits the incidence angle range of the infrared radiation illuminating the sample. Incidence angles between 49° and 85° are possible.

The simulated system (done with a ray-tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e., 13 % of the radiation passing through the first aperture (Ø 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (Ø 3.5 mm) on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, the efficiency is about 20x higher.

The performance of the system is demonstrated by first measurements.

[1] J. Pavelec, et al., J. Chem. Phys. 146, 014701 (2017).

10:00am **SS1+AS+HC-FrM-6 Photochemical Fluorination of TiO_2(110)**, ***Melissa Hines***, *W. DeBenedetti, Q. Zhu, M. Hasany, D. Somaratne,* Cornell University

Fluorine has been widely reported to improve the photoreactivity of TiO_2 nanocrystals, but surface science studies of this enhancement have been stymied by the lack of well controlled fluorination chemistries. Fluorine-terminated rutile (110) surfaces were produced by the photochemical degradation of solution-prepared carboxylate monolayers in the presence of XeF_2 (g) at room temperature. The reaction initially produces a multi-nanometer-thick surface layer with a nominal composition of $TiOF_2$. The $TiOF_2$ layer largely dissolves with immersion in room temperature H_2O, leaving behind a fluorinated surface terminated by 0.8 monolayers of F bound to initially undersaturated Ti atoms. Scanning tunneling microscopy images showed that the fluorinated surface was rough on an atomic scale, displaying short, atomically straight rows parallel to the [001] direction. The fluorinated surface remained notably contamination free, even after immersion in solution and exposure to air for tens of minutes. The relatively high reactivity of the $TiOF_2$ surface layer towards etching can be rationalized in terms of disrupted charge balance in the surface layer. Consistent with this, density functional theory simulations showed that the removal of bridging O atoms from the fully fluorinated surface to produce O_2 would be exoergic.

10:20am **SS1+AS+HC-FrM-7 Surface Structures of $La_{0.8}Sr_{0.2}MnO_3$ (001) Thin Films**, ***Erik Rheinfrank***, *M. Brunthaler, G. Franceschi, M. Schmid, U. Diebold, M. Riva,* Institute of Applied Physics, TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved already for the (110) orientation [1,2]. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films were transferred in UHV from the PLD chamber to a surface science system, and characterized with scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low-energy electron diffraction. We show how the LSMO surface structures change due to variation of the oxygen chemical potential upon annealing. Moreover, Ar^+ sputtering and subsequent annealing removes preferentially Mn over La. This can be exploited to transform a B-site (Mn) terminated surface into an A-site (La/Sr) rich surface. The B-site terminated surface is recovered by depositing Mn from an MnO target.

[1] Franceschi et al., J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi et al., Phys. Rev. Materials, 2021, **5**, L092401

10:40am **SS1+AS+HC-FrM-8 Adsorption of Organophosphate Nerve Agent VX on the (101) Surface of Anatase Titanium Dioxide**, ***Gloria Bazargan***, NRC Research Associate, U.S. Naval Research Laboratory; *I. Schweigert, D. Gunlycke,* Chemistry Division, U.S. Naval Research Laboratory

We quantify the adsorption of the organophosphate venomous agent X (VX) on the clean and hydroxylated (101) surfaces of anatase titanium dioxide (TiO_2) with density functional theory (DFT) calculations. Our results show that adsorption on the clean anatase (101) surface occurs through the VX phosphoryl oxygen (O=P) site and involves the formation of a Ti···O=P dative bond. Steric effects inhibit adsorption through the VX nitrogen and sulfur sites by the formation of Ti···N and Ti···S dative bonds. On the hydroxylated (101) surface, adsorption similarly proceeds through the VX phosphoryl oxygen site but entails the formation of surface–adsorbate hydrogen bonds. Additionally, weak non-covalent interactions between the surface hydroxyl groups and the adsorbate's nitrogen and sulfur atoms stabilize VX/(101) complexes formed by adsorption through these secondary sites.

Surface Science Division
Room 320 - Session SS2+CA+AS-FrM

Environmental, Atmospheric and Astronomical Surfaces

Moderators: Kathryn Perrine, Michigan Technological University, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:20am **SS2+CA+AS-FrM-1 Combining Synchrotron X-ray and SFG Spectroscopy Techniques to Illuminate Aqueous Interfaces**, *S. Nayak, R. Kumal, A. Carr,* Argonne National Laboratory, USA; *S. Lee,* Argonne National Laboratory; ***Ahmet Uysal***, Argonne National Laboratory, USA **INVITED**

Chemical separations are central to our energy, environment, and security needs. From efficient refinery and recycling of rare earths to cleanup of contaminated underground waters, chemical separations cover a wide range of processes such as liquid-liquid extraction (LLE), membranes, and sorbents. A common theme in most processes is that the target ions need to adsorb on or go through an interface. Understanding aqueous interfaces at molecular scale, require special experimental techniques that can distinguish the interfacial structures from the overwhelmingly larger bulk.

Surface sensitive synchrotron X-ray scattering and fluorescence, and vibrational sum frequency generation (SFG) spectroscopy techniques are among the most advanced tools available to study aqueous interfaces. Interestingly, these techniques have been developed in separate communities and there are only a handful of studies that take advantage of complementary nature of them. In this presentation, I will summarize our group's efforts in understanding aqueous interfaces in chemical separations, by combining these two experimental techniques. I will provide specific examples where a single method is not enough to decipher the complex interactions at the interface. The examples cover ion-amphiphile interactions in LLE [1-4] and ion adsorption on graphene-oxide thin films [5].

1. Nayak, S.; Kumal, R. R.; Liu, Z.; Qiao, B.; Clark, A. E.; Uysal, A., Origins of Clustering of Metalate–Extractant Complexes in Liquid–Liquid Extraction. ACS Appl. Mater. Interfaces 2021, 13 (20), 24194-24206.

2.Kumal, R. R.; Nayak, S.; Bu, W.; Uysal, A., Chemical Potential Driven Reorganization of Anions between Stern and Diffuse Layers at the Air/Water Interface. J. Phys. Chem. C 2021.

3.Kumal, R.; Wimalasiri, P.; Servis, M.; Uysal, A., Thiocyanate Ions Form Antiparallel Populations at the Concentrated Electrolyte/Charged Surfactant Interface. ChemRxiv 2022, https://doi.org/10.26434/chemrxiv-2022-x8s7x

4.Nayak, S.; Kumal, R. R.; Uysal, A., Spontaneous and Ion-Specific Formation of Inverted Bilayers at Air/Aqueous Interface. Langmuir 2022, https://doi.org/10.1021/acs.langmuir.2c00208

5.Carr, A. J.; Kumal, R. R.; Bu, W.; Uysal, A., Effects of ion adsorption on graphene oxide films and interfacial water structure: A molecular-scale description. Carbon 2022, 195, 131-140.

9:00am **SS2+CA+AS-FrM-3 X-Ray Studies of Extractant and Lanthanide Ion Ordering at Liquid Interfaces Relevant to Solvent Extraction***, **Mark Schlossman**,* University of Illinois at Chicago **INVITED**

Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. Complexation of metal ions with extractants and complexants is believed to take place at or near the organic-aqueous interface, as demonstrated recently by synchrotron x-ray measurements which locate and characterize metal ions and their complexes in the liquid-liquid interfacial region. This presentation will describe recent X-ray studies of model liquid interfacial systems relevant to the extraction of rare earth ions. These results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction kinetics.

9:40am **SS2+CA+AS-FrM-5 Probing Surface Chemistry in Complex Environments: Water Disinfectants and Ionic Solutions at the Air/Liquid/Iron Interface***, **Kathryn Perrine**,* Michigan Technological University

Water disinfectants are used to treat pathogens in the water supply, but chlorine is known to react with organic matter to produce toxic disinfectant by-products (DBP). Other disinfectants, such as monochloramine, provide a higher level of disinfection without producing chlorinated DBP's. However, studies have shown that monochloramine can corrode copper and lead surfaces, but little is known for iron-based materials. Iron interfaces are prevalent in soils, minerals, and atmospheric dust, and are known to undergo redox reactions. Iron is a known catalyst in several processes due to its different active sites. Due to the advent of degradation of disinfectants in the water supply, the reaction of monochloramine was investigated on iron interfaces in complex environments.

The interaction of monochloramine was studied at the air/solution/iron interface using *in situ* polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS). These studies are compared with the iron interfaces exposed to aqueous solutions that were used to synthesize monochloramine, NH_4Cl(aq), NaOH(aq), and NaOCl(aq). After exposure to each solution, ATR-FTIR spectroscopy and X-ray photoelectron spectroscopy were used to measure the chemical composition at the interface region exposed to atmospheric O_2 and CO_2 and the region submerged in solution. This builds upon our previous work where we have investigated alkali and alkaline chloride solutions at the air/electrolyte/iron interface. There the anion acts to corrode the surface to produce nucleation sites for carbonate film growth, while the cation influences the mineral film identity and the rate of carbonation from the uptake of CO_2. These findings show that water disinfectants at solution/metal interfaces result in unexpected reactions in complex aqueous systems, which may provide insight for related surface catalytic and environmental processes.

10:00am **SS2+CA+AS-FrM-6 The Surface Chemistry of Martian Mineral AnalogsDuring Triboelectric Charging in Sand Storms***, **Mikkel Bregnhøj**, T. Weidner, K. Finster,* Aarhus University, Denmark

The surface chemistry of the Martian regolith has a significant impact on the atmospheric composition on the Red Planet. For example, methane concentrations vary by a factor of ~3 or more during a Marsian year. Theories based on established photochemical and environmental mechanisms, have so far failed to accurately model the seasonal variation. The currently known gas/solid interfacial chemistry that forms and removes methane from the Marsian atmosphere is insufficient to explain the observed dynamics.

We propose an alternative driver of Martian surface chemistry: wind-driven triboelectric charging of minerals. Sand storms, saltation, and erosion are common phenomena on the Red Planet. In proof-of-principle laboratory experiments, we have shown how Martian mineral analogs can erode each other and induce electric discharges with sufficient energy to (1) ionize and/or dissociate gasses like argon, methane, and carbon dioxide and (2) drive gas/solid interfacial chemistry of organic species present on the surface of these minerals. Using advanced surface spectroscopies (XPS, NEXAFS, etc.) we show how saltation can drastically alter the gas and mineral surface composition. For example, tumbling quartz sand in a methane atmosphere will change the colour of the sand from pristine white to reddish/brown (see attached figure). Using a custom-built container, we also simulate a sand storm with realistic Martian atmospheres and mineral analogs, sealed inside a container made of the very same mineral. In this way, we exclude possible interference effects from the container walls, and come as close to the actual conditions of a sand storm on Mars as is possible on Earth.

10:20am **SS2+CA+AS-FrM-7 Unraveling Water Formation on Planetary and Astrophysical Bodies: The Role of Surface Science***, T. Orlando, **Brant Jones**,* Georgia Institute of Technology **INVITED**

The sources of molecular water in planetary systems is a subject of general interest in astrophysics and astrochemistry and its presence and persistence are critical for life on Earth and for space missions involving long term human exploration.The Moon is the nearest exploration target and sources of water include primordial water, delivery via comets and meteorites, formation and release during small impact events, and solar wind interactions. Our controlled surface science experiments have demonstrated that thermally activated recombinative desorption (RD) or associative desorption (AD) from lunar regolith and other solar wind irradiated grains can be an additional source term for water formation. This involves hydroxyl (-OH) defects made by implantation of solar wind protons. Using several Apollo lunar samples, temperature program desorption (TPD) experiments conducted under ultra-high vacuum conditions yielded first order activation energies for desorption of chemisorbed molecular water and second order activation energies for the RD mediated formation and release of molecular water. Depending on the temperature excursions, RD can occur on a diurnal basis on the Moon and is likely prevalent during impacts with meteorites and meteoroids. This is simulated by laser impact studies followed by state and velocity resolved detection of the photo-produced water. Once formed, the water can either desorb, or be transported on and within the regolith and grain surfaces.Our combined experimental and modeling effort has successfully simulated recent observational data of water on both Mercury and the Moon. Water formation via RD is also likely general under astrophysical conditions that involve proton bombardment followed by thermal excursions (> 400 K), and is critical to the formation of water in star forming regions and in developing strategies for extraction of water for future, sustainable human space exploration missions.

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