

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 Line¹. 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 thickness². 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 plasma³.

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 SiO₂ Surfaces**, **Anthony Valenti**, C. Vallée, C. Ventrice, SUNY Polytechnic Institute, Albany; *K. T opilý, 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 SiO₂ surfaces versus Si and non-oxidized metal surfaces, these precursors can be used to block deposition of metals on SiO₂ 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 SiO₂ surfaces passivated via exposure to TMSDMA, including ozone exposure, H₂ plasma treatment, and H₂ plasma treatment followed by H₂O vapor exposure. This project also explores using a second inhibitor dosing via NF₃ plasma treatment in order to fluorinate any nucleation sites left vacant on the SiO₂ 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. Merckx, 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 SiO₂ inhibition on the Al₂O₃ 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 SiO₂ 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.

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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 $98.4 \pm 0.2\%$ could be achieved by dosing HAC and Hthd sequentially, which is higher than either $96.0 \pm 0.6\%$ by Hthd or $97.0 \pm 0.5\%$ 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. Merckx *et al.*, J. Phys. Chem. C 126, 4845 (2022).

[3] M.J.M. Merckx *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 Merckx¹, 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-butylimidodis(dimethylamino)tantalum (TBTDMT) as the precursor molecule, and (C) an Ar-H₂ plasma as the co-reactant. This process was found to selectively deposit TaN on dielectric surfaces (e.g. Al₂O₃ and SiO₂) 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 Al₂O₃, 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 NH₃ while benzene remains adsorbed on the surface. This reaction eliminates the NH₂ 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] Merckx *et al.*, Atomic Limits 7, (2022) <https://www.atomiclimits.com/2022/04/18/>

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

[3] Merckx *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 SiO₂ 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 SiO₂. With this strategy, we demonstrate AS-ALD of ZnO and Al₂O₃ on Cu (growth surface) over SiO₂ (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 SiO₂-covered Si substrate) and 15 cycles of Al₂O₃ ALD (corresponding to 1.4 nm of Al₂O₃), 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 Wojtecki⁴, 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 diene 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.

¹ 2021 TFD James Harper Awardee

² TFD James Harper Award Finalist

³ AVS Russell and Sigurd Varian Awardee

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⁴ Peter Mark Memorial Award Winner

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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 octahedrane, 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 (Cr₂O₃). During aqueous corrosion, a complex surface layer containing Ni(OH)₂, Cr(OH)₃, and Cr₂O₃ 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/cm²) 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 Cr₂O₃ 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 C2p_{3/2} peak shape, while for Mo 3d_{3/2} and Ni2p_{3/2} 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 NiFe₂O₄ 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 (NiFe₂O₄) thin films grown on Al₂O₃. 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 Pt₃Ni(111) and Pt₃Co(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 Pt₃Ni(111) and Pt₃Co(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 Pt₃Ni and Pt₃Co 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 a 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 H₂O 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.

**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 Diaz*, 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 fast-molecule diffraction (GIFMD), on the other hand, has received much less attention (mostly theoretical^{5,6}), despite the fact that the H₂ molecule: (i) is as easy to generate as atomic H (a widely used projectile in GIFAD experiments); (ii) is lighter than He (another widely used projectile in GIFAD), which would further reduce surface-phononinelastic processes; and (iii) can reveal aspects of the surface landscape that may be relevant in other contexts due to the internal degrees of freedom (DOFs) and, in the case of the ionic surfaces, to the interaction of its quadrupole moment with the electric field created by the ionic crystal, which is very sensitive to the surface details. Here, we present a theoretical study of grazing-incidence fast-molecule diffraction of H₂ from KCl(001) using a six-dimensional density functional theory based potential energy surface and a time-dependent wavepacket propagation method. The analysis of the computed diffraction patterns as a function of the molecular alignment, and their comparison with the available experimental data, where the initial distribution of rotational states in the molecule is not known, reveals a puzzling stereo dynamics effect of the diffracted projectiles: Diffracted molecules aligned perpendicular, or quasi perpendicular, to the surface reproduce rather well the experimental diffraction pattern, whereas those molecules aligned parallel to or tilted with respect to the surface do not behave as in the experiments. These results 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**, *Svetlana Schauerma*, 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.

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2. Attia, S. et al *ACS Catal.* **2019**,9, 6882.
3. Attia, S. et al, *J. Phys. Chem. C* **2019**,123 (48), 29271.

9:20am **SS+AS+TF-MoM-4 Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)**, *Arved Cedric Dorst*, T. Schäfer, University of Göttingen, 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_2 gas 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 (Cr_2O_3) 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 Tunneling 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

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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 Sinnott¹**, 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 Alupotha Gedara², 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.

¹ Medard W. Welch Award Winner

² SSD Morton S. Traum Award Finalist

Monday Afternoon, November 7, 2022

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 WTe₂(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 WTe₂, 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 WTe₂(001) surface as both a function of coverage and temperature. XPS measurements of the WTe₂(001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of PdTe₂ 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 WTe₂(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 WTe₂(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:WS₂ 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 WS₂ 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 WS₂ 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 WS₂ 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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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 Nanofibrous H-Type MnO₂ 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), which has enabled its use in catalysis², energy storage³, and gas sensing⁴. Of these manganese oxide compounds, manganese dioxide (MnO₂) 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 MnO₂. In particular, the Mn⁺³ defect density, which has been found to increase the reactivity of the MnO₂ film⁶, is highly variable between polymorphs, with the δ phase exhibiting the highest defect density. Water stabilized δ-MnO₂ (H-δ-MnO₂) 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 defects⁷. However, the production of H-δ-MnO₂ has proven challenging in the literature. In this work, we present the synthesis of H-δ-MnO₂ 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-MnO₂ and probe its surface morphology. The Raman spectra indicated the successful formation of H-δ-MnO₂, 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-MnO₂ 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-MnO₂ 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 transduction¹, which can be exploited for modular memory and logic devices. Ferroelectric switching has been previously demonstrated in bilayer and trilayer WTe₂²⁻⁴, where the polarity can be controlled by electric gating. VdW based semiconducting FMs, such as Cr₂Ge₂Te₆ (CGT), provide the opportunity to study tunable magnetic phenomena and to build superlattices with other quantum materials⁵. By coupling a semiconducting ferromagnet to a Weyl semimetal, magnetization can be induced at the interface by magnetic proximity effect. We have fabricated WTe₂/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 WTe₂ 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

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.

[1] D. Nowak et al., Sci. Adv. 2, e150157 (2016).

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

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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. Al₂O₃ ALD experiments using TMA and O₂ plasma validated this uniform front propagation model. A smoothing rate of 5.5·10⁻³ nm RMS roughness reduction per nm of deposition was determined, revealing that significant smoothing by ALD requires relatively thick films (e.g. > 20 nm).

Al₂O₃ ALE from TMA and SF₆ plasma³ resulted in a larger roughness reduction of 9.8·10⁻³ 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.

(1)Elam *et al.*, *Thin Solid Films***414**, 43 (2002)

(2)Zywotko *et al.*, *J. Vac. Sci. Technol. A* **36**, 061508 (2008)

(3)Chittock *et al.*, *Appl. Phys. Lett.* **117**, 162107 (2020)

3:00pm AP+AS+EL+MS+SS-MoA-5 Thermal Atomic Layer Etching of Amorphous Aluminum Nitride Using SF₆ Plasma and Al(CH₃)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 SF₆ plasma and trimethylaluminum (Al(CH₃)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 SF₆ 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°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 MoS₂ 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 (MoS₂) 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 MoS₂ 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 MoS₂ 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

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investigate area selectivity. MoS₂ 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 MoS₂ 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 Al₂O₃ and AlF₃ using Wafer Curvature Techniques, Ryan B. Vanfleiter, 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 (Al₂O₃) ALD using trimethylaluminum (TMA) and H₂O as the reactants was used as a model system to test this new apparatus. Al₂O₃ ALD was explored at different deposition temperatures ranging from 130 to 285°C. The in situ measured film stress during Al₂O₃ 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 Al₂O₃ ALD film stresses are in good agreement with ex situ film stress measurements for Al₂O₃ 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 H₂O 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 AlF₃ ALD using TMA and HF as the reactants. AlF₃ ALD showed similar surface stress behavior to Al₂O₃ 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 AlF₃ ALD temperatures between 150-200°C, the compressive surface stress resulting from the TMA exposures is ~0.45 N/m. In marked contrast to Al₂O₃ ALD, AlF₃ ALD displayed no film stress during film growth. This lack of film stress in AlF₃ ALD films may be related to the nature of the AlF₃ ALD film as a molecular solid.

[1]O.M.E. Ylivaara et al., *Thin Solids Films* **552**, 124 (2014)

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/HfO₂/SiO₂/Si as well as more complex stacks such as TaN/TiAl/TiN/HfO₂/SiO₂/Si or W/TiN/HfO₂/SiO₂/Si. Results will be presented obtained both with Cr K α (5.4 keV) and Ga K α (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.

References

[1]<https://www.ulvac-phi.com/en/products/xps/quantex/>

[2]<https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument>

[3]<https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab>

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 Acquisition 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 facilities 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 2p 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 3d 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.

[1] D. Cabrera-German, G.-B. Dulce-Maria, M. Mayorga-Garay, O. Cortazar-Martinez, J.-A. Torres-Ochoa, A. Carmona-Carmona, A. Herrera-Gomez, Peak and background parameters of the 2p core level of the pure first row transition metals, *J. Vac. Sci. Technol. A.* (2022) (in progress).

[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>.

[4] J.E. Castle, a. M. Salvi, Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* 19 (2001) 1170. <https://doi.org/10.1116/1.1378074>.

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 simultaneous 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

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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].

[1] L. Edwards, P. Mack and D. J. Morgan, "Recent advances in dual mode charge compensation for XPS analysis". *Surface and Interface Analysis*, 51 (2019) 925-933

[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**, *Benjamin 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 K α 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 $\pm 6.5\%$ 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-methylimidazolium-bis(trifluoromethyl sulfonyle)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 the TopoChip[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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[3] Immune modulation by design: using topography to control human monocyte attachment and macrophage differentiation Vassey et al. **Advanced Science** 7 (11), 1903392 (2020).

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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 University, 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

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pulsed a square wave at 15 μ s 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 μ L/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 hindrance in fully-dense PCysMA brushes limits binding of bulky chlorophylls, but the chlorophyll concentration can be increased to $\sim 2M$, 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 (\sim 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, Svetlana Schauer mann, Christian-Albrechts-University Kiel, Germany

2:00pm **HC+AS+SS-MoA-2 Electro catalytic 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 $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ 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 Electro catalytic 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

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(Haber-Bosch). Catalysts requirements for this reaction, however, are immense: water/protons are required to reduce nitrate but compete with NO₃RR to evolve hydrogen gas at comparable potentials, and selectivity along an 8 e⁻/10 h⁺ process is required to produce ammonium. Here we investigate NO₃RR 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 NO₃RR 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 NO₃RR 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. Rumpitz, 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/m² 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/m² 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/m². 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/m².

5:00pm **HC+AS+SS-MoA-11 Size Dependent CO₂ 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 CO₂ reduction reaction (CO₂RR). Size-dependent CO₂RR activity of Au and Cu has been studied, and increased H₂ 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 CO₂RR activity and selectivity of Ag nanoparticle electrocatalysts in the sub-5 nm range. Experimental results identified CO₂RR 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 CO₂RR activity and selectivity. A nearly identical size-dependent trend was also predicted in computational modeling: smaller diameter particles favored H₂ evolution reaction (HER) due to a high population of Ag edge sites, whereas larger diameter particles favored CO₂RR as the population of Ag(100) surface sites grew. Our results resolve the CO₂RR 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 CO₂RR activity of pristine Ag catalysts and will help guide future catalyst development efforts.

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. We want to show how information from SFG spectroscopy can be coupled with molecular dynamics simulation to resolve molecular 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 information like interactions with per residue resolution and the nature of their vibrations at the interface is gained by calculating 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 that α-helical peptides lying flat on an interface mainly interacts with surface with the residues on the side of the helix. The top and bottom positioned residues are more rigid and despite the bottom residues' close proximity to the surface, they are not as highly perturbed by the presence of the interface.

Furthermore, SFG allows us 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

¹ SSD Morton S. Traum Award Finalist

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 ordinarily 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)- $p(1 \times 1)O$ (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)- $p(1 \times 1)O$ 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_1 TPP + M_2 TPP monolayers were grown sequentially at room temperature by depositing x ML of M_1 TPP on Fe(001)- $p(1 \times 1)O$ followed by $(1-x)$ ML of M_2 TPP (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_1 TPP) is deposited first ($x = 0.25$), followed by ZnTPP; bottom row: ZnTPP (M_1 TPP) 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)- $p(1 \times 1)O$. 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 Nb₃Sn 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. Nb₃Sn 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.

Nb₃Sn films are currently grown *via* Sn vapor deposition on preexisting Nb cavities. It is understood that the thickness of the native Nb pentoxide (Nb₂O₅), Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high Q film growth. There is not, however, an understanding of the Nb₃Sn 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 Nb₃Sn growth models needed for the further optimization of Nb₃Sn growth procedures.

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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 ((Me₃Ge)DHP) is a new reducing that is found more efficient than its earlier reported silicon analogue. NiCl₂(PEt₃)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 NiCl₂(PEt₃)₂ - (Me₃Ge)DHP combination affords deposition of Ni at 110 °C which is the lowest temperature for thermal ALD of Ni so far. (Me₃Ge)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 O₂ and H₂ 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 SiO₂, 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 TiO₂ Deposited by PEALD Assisted by Substrate Biasing on Thermal SiO₂ 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 deposed 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 processes².

PEALD TiO₂ 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 SiO₂ 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 TiO₂ 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 TiO₂ thin films on TiN against SiO₂.

References

1. C. Vallée, M. Bonvalot *et al.*, J. Vac. Sci. Technol. A 38(3) May/June 2020
2. T. Faraz *et al.*, ACS Appl. Mater. Interfaces, 10, 13158-1318 (2018)

9:00am AP+AS+EM+HI+PS+SS+TF-TuM-4 Area Selective Atomic Layer Deposition of SnO₂ 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. Sn⁰-containing block copolymers were demonstrated as materials for nanolithographic applications.

Here we propose SnO₂ 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 SnO₂ grid patterns, which can be transferred into the Si native oxide substrate using SF₆ RIE. The concept is illustrated using a 1000-mesh copper TEM grid as an ultraviolet light shadow mask to generate patterns in polystyrene. SnO₂ patterns are achieved by area selective atomic layer deposition (ALD) using tetrakis(dimethylamino) tin(IV) and H₂O 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 SnO₂ 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. SnO₂ 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 SnO₂ grown on native oxide has a low roughness of 75 pm, while SnO₂ grown on H-terminated Si has a relative higher roughness of 250 pm indicating a 3-D growth process. To create SnO₂ patterns 20, 50, and 100 ALD cycles of SnO₂ are selectively deposited onto Si native oxide with estimated SnO₂ thicknesses of 1.2 nm, 3 nm and 6 nm, respectively. Samples are then etched with SF₆ RIE for 30 s to 1 min at room temperature and 200 mTorr. AFM results show that SnO₂ 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 SnO₂ is transformed into SnF₄ for 100 ALD cycle samples, while all of the SnO₂ is transformed into SnF₄ 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 -CH₃, -OH and -COOH terminated self-assembled monolayers (SAMs). On -OH terminated SAMs, as the bath pH increases from 10 to 12, the tin sulfide

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deposited changes from SnS₂ to Sn₂S₃. On -COOH terminated SAMs the deposit is S₂S₃ at pH 10 and SnS at pH 12. In contrast, on -CH₃ terminated SAMs the deposit changes from SnS at pH 10 to Sn₂S₃ 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/-CH₃ terminated SAMs. We term this method Semiconductor Nanowire Deposition On Micropatterned substrates (SENDOM). In SENDOM the deposition reaction is kinetically favored on the -CH₃ 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 -CH₃ terminated surfaces.

9:40am **AP+AS+EM+HI+PS+SS+TF-TuM-6 Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO₂ Films 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 TiO₂ by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and O₂ 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, TiO₂ 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 TiO₂ on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 °C to 200 °C, and O₂ 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 O₂ plasma as an oxidant resulted in anatase TiO₂ films irrespective of thickness, even when deposited at temperatures below 100 °C. However, the anatase phase is significantly weaker when H₂O is used as the oxidant. An interfacial layer of ALD Al₂O₃ 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 TiO₂. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous TiO₂. This fluorine on the surface of the carbon paper serves as a directing agent¹⁻⁵ for the application of TTIP to PTFE in a fluorolysis reaction, which drives the TiO₂ to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize TiO₂ powders.^{6,7} Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO₂ films. With this strategy, surface initiation chemistries can be used to achieve area-selective and in situ crystallization 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 In₂O₃. 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 Ga₂O₃ ALD nucleation on TiO₂ single crystals and MgO ALD on In₂O₃ broadly 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 H₂. The Pd ALD reaction proceeds in the presence of atomic hydrogen; Pd growth nucleates without delay on a Ni metal seed layer that catalyzes H₂ dissociation. Once nucleated, the evolving Pd surface catalyzes H₂ 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 H₂O 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 Ni⁰, effectively seed Pd growth through catalytic area activation. NiO reduction employs an e-beam heated tungsten capillary at 2.5 × 10⁻⁶ Torr H₂ 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 O₂ 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 O₃) 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

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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 N₅-edge identify a bulk, UO₂ 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 to 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 initio* treatment of the main and satellite features in the cation 2p XPS of Fe₂O₃ 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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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*, DENSolutions, 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 be 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 K α 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

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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 HfO₂. 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 K α (1486.6 eV) and a Cr K α (5414.8 eV - *Quantes*) or Ga K α (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 IO14018N.

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 discoordination¹⁻². 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 (H₂O)_n (_{n>28k})-GCIB-SIMS and C₆₀-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 μ m resolution. The novel ion source, (H₂O)_n(_{n>28k})-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to *m/z* 6000³⁻¹². 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 survival²⁷. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue³⁷. 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 Chiamonti, 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.

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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 TiO₂(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 TiO₂ 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 TiO₂(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 tunneling microscopy measurements on single-crystal TiO₂ 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 TiO₂. The reaction of bidentate acetate produces ketene and water as determined by temperature-

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programmed reaction spectroscopy on single-crystal TiO₂. 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 TiO₂ 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 TiO₂ catalysts.

9:00am HC+AS+SS-TuM-4 Phase Transformation of Single Micro-Sized TiO₂ Crystals, *W. Lu, H. Zhu, N. Craft, K. Park, Zhenrong Zhang*, Baylor University
Understanding the reactivity of various crystal faces in different polymorphs of TiO₂ in photoreaction is important for many photocatalytic applications. Here, we monitored and studied the anatase-rutile phase transition (ART) processes of individual micro-sized TiO₂ crystals from the pure anatase phase to the mixed-phase, then to the rutile phase. High-quality micro-sized anatase TiO₂ 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 Fe₃O₄(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 Fe₃O₄(001) under ultrahigh vacuum conditions. The single Rh adatoms are found to be the most active towards CO₂ production, followed by incorporated Rh and then by Rh nanoclusters. While the reaction of formic acid with Fe₃O₄(001) primarily results in CO desorption at ~570 K, the addition of small amounts of single adatom Rh (~0.01 Rh per Fe₃O₄(001) unit cell (u.c.)) results in a dramatic shift towards CO₂ production at lower temperatures starting at 540 K and dropping to ~470 K at larger HCOOH coverages. The incorporated Rh system also yields CO₂ 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 CO₂ and H₂ desorption at ~310 K while still producing substantial amounts of CO₂ at 450-500 K, not observed on pure Fe₃O₄(001). These differences demonstrate that different forms of Rh supported on Fe₃O₄(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 Fe₃O₄(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 CO₂ activity.

9:40am HC+AS+SS-TuM-6 WO₃/Ag₂S 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, WO₃/Ag₂S 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 WO₃ deposited using DC sputtering and a well-separated Ag₂S nanorods fabricated by glancing angle deposition. The PEC response was studied for bare WO₃, Ag₂S, and WO₃/Ag₂S heterojunction. The as-prepared WO₃/Ag₂S heterojunction samples revealed higher absorption as well as higher photocurrent density of 2.40 mA/cm² (at 1V Ag/AgCl) as compared to bare WO₃ thin film (0.34 mA/cm²). The enhancement in the photocurrent density of WO₃/Ag₂S electrodes could be ascribed to the formation of the type-II heterojunction between WO₃ and Ag₂S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag₂S nanorods structures results in an effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that WO₃/Ag₂S 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 WO₃ and Ag₂S 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 TiO₂(110), *Greg Kimmel*, Pacific Northwest National Laboratory INVITED

TiO₂ 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 splitting, it has been the subject of a tremendous amount of research. We have investigated the photon-stimulated reactions of small molecules, such as O₂, CO, and acetone, on rutile TiO₂(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 O₂, 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 CO₂ 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 Fe₂O₃ Model Support, *Gareth Parkinson, A. Rafsanjani Abbasi, L. Puntsher, 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. Fe₂O₃ 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 (1x1) termination of Fe₂O₃(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.

¹F. Kraushofer *et al.*, Single Atom Catalysts: Surface Reduction State Determines Stabilization and Incorporation of Rh on α -Fe₂O₃(1-102) (Adv. Mater. Interfaces 8/2021). *Advanced Materials Interfaces* **8**, 2170045 (2021).

²F. Kraushofer *et al.*, Single Rh Adatoms Stabilized on α -Fe₂O₃(1102) by Coadsorbed Water. *ACS Energy Letters* **7**, 375-380 (2022).

³F. Kraushofer *et al.*, Atomic-Scale Structure of the Hematite α -Fe₂O₃(1-102) "R-Cut" Surface. *J. Phys. Chem. C* **122**, 1657-1669 (2018).

⁴G. Franceschi *et al.*, A Model System for Photocatalysis: Ti-Doped α -Fe₂O₃(1-102) Single-Crystalline Films. *Chem. Mater.* **32**, 3753-3764 (2020).

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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 Fe₃O₄(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 Fe₃O₄(001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe₃O₄(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 Fe₃O₄ surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO₂ 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, CO₂ interacts most weakly with Rh adatoms and nanoparticles, while interactions between Rh-octahedral and Fe-octahedral are indistinguishable. Further, CO₂ is used to distinguish between metallic Rh sites and Fe₃O₄(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.

Surface Science Division

Room 319 - Session SS-TuM

Liquid/Solid Interfaces and Electrochemistry

Moderators: Kathryn Perrine, Michigan Technological University, Michelle Personick, Wesleyan University

8:00am **SS-TuM-1 Investigating the Oxidation of Pt(111) Using High-Pressure Scanning Tunneling Microscopy, Force Field Calculations, and Ab Initio Thermodynamics**, *D. Boden*, Leiden University, Netherlands; *M. van Spronsen*, Diamond Light Source, UK; *J. Frenken*, ARCNL; *J. Meyer, Irene Groot*, Leiden University, Netherlands

Platinum has always been an important catalyst for oxidation reactions in the automotive industry, but also for electrocatalysis. Therefore, oxidation of and on platinum surfaces has long been a favorite topic in the field of surface science. Recently, the development of in situ and operando techniques has shown that the classic ultrahigh vacuum (UHV) approach is inadequate to describe the catalyst at realistic catalytic conditions. We will show that under these conditions (>530 K and >1 bar O₂), the Pt(111) surface oxidizes and forms spoke wheel and stripe-like structures that are not stable under UHV conditions. The striped structures we found using high-pressure scanning tunneling microscopy have since been investigated using a combination of density functional theory (DFT) and ab initio thermodynamics (AITD) to evaluate the surface free energy at realistic temperatures and pressures. Here we do the same for the spoke wheel structure. However, since even the smallest candidate structures are too large for ordinary DFT calculations, we employ a ReaxFF force field developed specifically for Pt and O. This force field is able to accurately reproduce results from DFT and allows us to obtain an atomic model for the spoke wheel structure that matches the experimental results closely. Using AITD we compare its relative stability to the stripe structures over a large range of temperatures and pressures. We show that the spoke wheel structure is more stable than the stripe structure if the surface is partially oxidized, while the stripe structure is more stable only if it covers the entire surface.

8:20am **SS-TuM-2 Operando Electrochemistry: NAP-XPS on Electrolyte/Electrode Interfaces - Studies of Liquid Electrolytes and Their Interfaces to Battery Cathodes for Lithium Ion Battery Applications, Francesca Mirabella**, *P. Dietrich, A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany

In this work, we present NAP-XPS results from model and commercial liquid electrolytes for lithium-ion battery production using an automated laboratory NAP-XPS system. As electrolyte solutions, we used LiPF₆ in EC/DMC (LP30) as a typical commercial battery electrolyte and LiTFSI in PC as a model electrolyte. We analyzed the LP30 electrolyte solution, first in its vapor and liquid phase to compare individual core-level spectra. In a second step, we immersed a V₂O₅ single crystal as a model cathode material in this LiPF₆ solution. Additionally, the LiTFSI electrolyte model system was studied to compare and verify our findings with previous NAP-XPS data. Photoelectron spectra recorded at pressures of 2–10 mbar show significant chemical differences for the different lithium-based electrolytes.

8:40am **SS-TuM-3 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Infrared Nanospectroscopy for Solid-Liquid Interface, Xiao Zhao^{1,2}, M. Salmeron**, LBNL

Nanoscale properties and dynamical processes at solid-liquid interface are critical for many natural phenomenon and industrial applications, including energy storage, self-assembly and corrosion. However, fundamental study of those processes is often challenged by radiation damage from electron or X-ray probe, which may drive the structure and chemical states of interface away from its original state. Herein we demonstrate a new non-destructive platform that enables nanoscale interfacial sensitive Infrared (IR) spectroscopy for solid-liquid interface by combining graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). With that we investigated the nanoscale structural evolution and response of protein assemblies to external environments as well as dynamical interaction between nanoparticles with ligand capping layer for CO₂ electroreduction. The protein substructure and ordering, and specific adsorption configuration of ligand on nanoparticles are monitored by their characteristic IR vibrational bands at nanometer scale under realistic condition, which provides complimentary information to other operando techniques. Our platform opens broad opportunities for operando study of soft materials or nanostructures (membrane protein, virus, nanoparticles and plastic material) in their realistic condition and under external stimuli.

9:00am **SS-TuM-4 Methods for Exposing UHV-prepared Metal Oxide Surfaces to Liquid Water: A Comparison of TiO₂, Fe₂O₃, and Fe₃O₄, Jiri Pavelec**, *J. Balajka, F. Kraushofer*, Vienna University of Technology, Austria; *Z. Jakub*, CEITEC, Czechia; *G. Franceschi, M. Schmid, G. Parkinson, U. Diebold*, Vienna University of Technology, Austria

The importance of bridging the pressure gap in studies of model catalysts has been recognized for decades. The investigation of surfaces under ambient conditions remains a challenge due to the restricted number of experimental techniques available and a high risk of contamination. The design of two working instruments for tackling the pressure gap in surface science will be presented: An apparatus for dosing liquid water in an ultrahigh vacuum [1,2] and a high-pressure cell [4]. The first instrument allows dosing a droplet of ultrapure liquid water on the surface of a sample without exposure to air. The second presented instrument is a novel design of a high-pressure cell, intended to expose metal-oxide single crystals to water vapour pressure up to the mbar range and elevated temperatures. Both instruments are coupled to an existing surface-science chamber, enabling reproducible sample preparation and sample characterization using UHV-based analytical techniques (q+AFM, XPS, LEIS). By exposing a number of metal oxides to liquid water we have learned that some surfaces stay intact, some are slightly modified, while some are completely changed. For example, no change is found after water drops or vapour exposure to rutile TiO₂(110) [2], and it can be utilised as a benchmark system for clean liquid water dosing. The α-Fe₂O₃(1102) surface exchanges oxygen with vapor and liquid water, but retains the UHV structure [3]. A more significant change was observed for Fe₃O₄(001): Multi-Langmuir water doses do not change a (√2 × √2)R45° reconstruction under UHV conditions, but liquid water at room temperature lifts the reconstruction [4] followed by the formation of a partial oxyhydroxide layer.

References:

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¹ SSD Morton S. Traum Award Finalist

² AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient

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 [4] F. Kraushofer, F. Mirabella, J. Xu, J. Pavelec, J. Balajka, M. Müllner, N. Resch, Z. Jakub, J. Hulva, M. Meier, M. Schmid, U. Diebold and G. S. Parkinson (2019). The J. Chem. Phys. 151:154702.

9:20am SS-TuM-5 Interplay of Structure, Dynamics and Energetics of Alkali Metal Ions on Muscovite Mica Surfaces: Molecular Dynamics Simulation, Alper T. Celebi, Vienna University of Technology, Austria; S. Reindl, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; M. Olgıati, Vienna University of Technology, Austria; T. Bauer, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; L. Maers, M. Valtiner, Vienna University of Technology, Austria

Adsorption of ions at the solid-liquid interface is of great importance in various physical processes such as corrosion of metals, electrochemical energy storage, swelling of clays, biofouling in the marine environment and transport in shale rocks. In these processes, the type of cation in an electrolyte solution has a profound influence on the hydration structure, dynamics and energetics of the ions at the interface. Atomistic simulations are practical to properly explore such influences at the molecular resolution. In this study, we performed molecular dynamics (MD) simulations of different aqueous salt electrolytes confined between two negatively charged mica surfaces. As the electrolyte, we used chlorides of different alkali metals, namely Cs⁺, K⁺, and Li⁺. We explored the variations in interfacial water density, ion concentrations, structural orientations, ion mobilities and hydration energies. Our simulations show that Cs⁺ has prominent concentration peaks at the surface, indicating very strong ion adsorption. Unorthodoxly, there are more counter-charges at the interface than is on the mica surface, which result in non-classical charge overscreening. However, this is not the case for Li⁺ ions. They bound less strongly to the surface. Thus, Li⁺ concentrations at the interface are lower than for Cs⁺ and K⁺ at the same molar concentration. This behavior is further supported by the ion mobilities at the interface where Cs⁺ ions are found to be more stagnant while Li⁺ ions are more mobile and K⁺ ions have intermediate characteristics. Another interesting finding is that Cs⁺ and K⁺ ions predominantly sit at the cavity center of muscovite mica, creating a diamond-shape pattern. On the contrary, Li⁺ cations are located on the charged oxygen site of the mica with slit-like formation. We assess that such structural orientations are mainly due to the differences in the ion sizes and electron densities. Moreover, water densities for Li⁺ solution show the most pronounced oscillatory layering at the interface. Although there are less Li⁺ ions at the surface compared to K⁺ and Cs⁺, more water molecules come near to the surface depleting the center of the channel for Li⁺ case. This clearly points out that hydration forces are more effective for the aqueous Li⁺ solution while the surface and metal ion interactions are the driving forces of Cs⁺ and K⁺ solutions. We also found out that the effect of the molar concentration has a negligible role on structure and energetics of mica and electrolyte interfaces. High-resolution atomic force microscopy imaging is being performed in parallel to further support our MD simulations.

9:40am SS-TuM-6 Corrosion Mechanism of Aluminum Alloy at Grain Boundaries Investigated by in-Liquid Nanoscale Potential Measurement Technique, Shinnosuke Yamamoto, D. Taniguchi, T. Okamoto, K. Hirata, Kanazawa University, Japan; T. Ozawa, Kobe Steel, Ltd., Japan; T. Fukuma, Kanazawa University, Japan

Al-Zn-Mg alloys are used as a structural material for automobiles and aircraft due to their outstanding strength. However, the high susceptibility to the local corrosion and stress corrosion cracking of the Al-Zn-Mg alloys limits their applications. The high susceptibility of Al-Zn-Mg alloy to the local corrosion is caused by the microstructural inhomogeneities such as the grain boundaries (GBs) and intermetallic particles. Along GBs of these alloys, a line-shaped precipitate free zone (PFZ) made of aluminum is formed. In addition, inside the PFZ, granular precipitates made of MgZn₂ are distributed along the GBs. The coexistence of these different materials forms corrosion cells to induce corrosion at the GBs. However, nanoscale mechanisms of such corrosion have been elusive. To solve this problem, we have directly imaged the corrosion behavior near the GBs of Al-Zn-Mg alloys in liquid on a nanoscale using a local potential measurement technique referred to as open-loop potential microscope (OL-EPM) (Fig.1). We imaged the changes in topography and potential at the same location during and after replacing the solution from water to pH 2.2 H₂SO₄ solution by OL-EPM. At 28 min after the immersion of an Al-Zn-Mg alloy

sample, high potential spots were observed inside the GBs (Fig. 2 (a) and (b), red arrows), which probably correspond to the MgZn₂ precipitates. Meanwhile, the relatively low potential area around MgZn₂ precipitates should correspond to the PFZ (Fig.2 (a) dotted line). Previous studies showed that the high potential area has high corrosion activity. Thus, the observed high potential areas suggest the anodic dissolution of the MgZn₂ precipitates. Indeed, the height profiles measured across one of the precipitates reveal a 10 nm height decrease caused by replacing water with the H₂SO₄ solution (Fig.2 (c)). At 97 min, the bright spot was not observed at the GB (Fig.2 (b) (iii)). This disappearance suggests the complete dissolution of the MgZn₂ precipitate. Consequently, the PFZ area shows a lower potential than the surrounding matrix. In addition, small anodic and cathodic regions are formed all over the matrix, forming many local corrosion cells. The dissolution of these anodic areas increased the surface roughness as confirmed in the height profile shown in Fig.2 (c). Based on these observations, we found that the MgZn₂ and PFZ areas respectively serve as the anode and cathode in the initial stage of the corrosion at GBs. After the complete dissolution of MgZn₂ precipitates, the matrix starts to serve as an anode instead of the MgZn₂ precipitates.

11:00am SS-TuM-10 Identifying Available Adsorption Sites on Au-Ps Alloys by FTIR Spectroscopy and Monte Carlo Simulations, S. Manzi, Dep. de Física, Universidad Nacional de San Luis, Instituto de Física Aplicada, CONICET, Argentina; M. Bosco, M. Brites Helú, Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina; A. Baldo, Fac. de Ingeniería Química (FIQ), Universidad Nacional del Litoral (UNL), Argentina; S. Collins, Florencia Calaza, Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina

Available adsorption sites on the surface of bimetallic AuPd compounds were studied by comparison of experimental results of CO adsorption, used commonly as a probe site molecule, on catalysts (powders) AuPd/CZ (ceria-zirconia) prepared in a relation 1:1 (Au:Pd), and on catalyst model surfaces prepared over single crystals. On both systems the sites exposed for CO adsorption are modified by calcining or heating the material to specific temperatures, allowing surface and bulk Au and Pd reordering. The spectroscopy results from both systems present some degree of agreement supporting in this way the need for interdisciplinary research to study catalytic systems. Furthermore, the system was also characterized by Monte Carlo simulations, which give an explanation for the increased availability of Pd atop sites experimentally observed, by forming Pd chains across the surface and avoiding 3-fold site formation due to agglomeration of Pd atoms.

11:20am SS-TuM-11 Role of Chemisorbing Species in Growth at Liquid Metal-Electrolyte Interfaces Revealed by in Situ X Ray Scattering, Andrea Sartori, ESRF, France

Liquid-liquid interfaces offer intriguing possibilities for nanomaterials growth. Especially, growth at liquid metal surfaces has recently received renewed interest. Here, fundamental interface-related mechanisms that control the growth behavior in these systems are studied for the case of Pb halide compound formation at the interface between liquid mercury electrode and aqueous salt solutions, using in situ X-ray reflectivity and grazing incidence X-ray diffraction, supplemented by electrochemical measurements and optical microscopy. The nucleation and growth of these compounds at potentials in the regime of Pb de-amalgamation was investigated in NaX + PbX₂ (X = F, Cl, Br) to systematically explore the role of the halide species. X-ray reflectivity studies reveal the rapid formation of well-defined ultrathin precursor adlayers in Cl- and Br-containing solution. This adlayer formation is followed by subsequent quasi-epitaxial growth of Pb(OH)X bulk crystals, that are oriented with the c-axis along the surface normal. In contrast, growth in F-containing solution proceeds by slow formation of a more disordered deposit, resulting in random bulk crystal orientations on the Hg surface. A detailed structural analysis of the Pb(OH)Br and Pb(OH)Cl precursor adlayers reveals that they determine the orientation of the subsequently formed bulk crystals, with the arrangement in the adlayer providing a template. Together with our previous results on the pseudo-epitaxial growth of PbFBr on Hg (A. Elsen, et al., Proc.Nat.Acad.Sci., 2013, 110, 6663), these data reveal the decisive role of the interface chemistry, especially the strong chemisorption of the anions bromide and chloride, in steering the formation of these textured deposits at the liquid metal surface.

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11:40am **SS-TuM-12 In Situ Electrochemical STM Imaging of an Au Electrode Identifying the Active Sites during the Electrocatalytic Process, Yongman Kim**, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Y. Jeong*, Institute for Basic Science (IBS), Republic of Korea; *Y. Kim, J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Understanding the influence of surface structural features is important for guiding mechanistic proposals for electrocatalytic reactions of the electrode. However, atomistic knowledge of the actual active sites remains elusive, because of the complicated relationship between structural stability and catalytic activity. With this in mind, we have focused on the fundamentals of the electrocatalytic process, using in situ electrochemical STM, and on locating the real active sites, a longstanding issue. In this work, we present STM results on two-dimensionally well-ordered manganese porphyrin structures on Au(111). We show that manganese porphyrins are oxidized after water oxidation and promptly decompose into catalytically active species as bright protrusions. These newly formed active species have dramatically lost their catalytic activity, either by acid treatment, one of the oxide removal methods, or by deposition of phosphonic acid, one of the oxide-favoring materials. This confirms that the active species are composed mainly of manganese oxides as a water oxidation catalyst. We extended our study to examine the surface structural sensitivity of Au single crystals itself for electrocatalytic CO₂ reduction as a simple model study. As the most active electrocatalyst for CO₂ conversion into CO, Au(*hkl*) shows structural dependency on coordinated sites, such as the terrace of Au(111) and the steps of Au(332). Through real-time electrochemical STM measurements, we have confirmed that these are the actual active sites for CO₂ reduction. A remarkable finding of our work provides the molecular evidence for Au and modified-Au electrode's active sites, providing impetus for future application in water oxidation and CO₂ reduction catalysts, as the data establishes a relationship between catalytic activity and structural changes.

12:00pm **SS-TuM-13 Extreme Atomic-Scale Surface Roughening: Amino Acids on Ag on Au(111)**, *E. Cook, K. P.S. Boyd, M. Paszkowiak, Erin Iski*, The University of Tulsa

A clear description of how surface morphology is affected by the bonding of biomolecules, like amino acids, with metal surfaces is critical to identify due to the potential applications in microelectronics, medical devices, and biosensors. Amino acids (AAs) on clean Au(111) were previously observed to trap Au adatoms, eventually leading to the formation of one atom high metal islands whose area was related to the amino acid molecular weight. To better understand the role of surface identity, L-Isoleucine on Au(111) modified with a Ag thin film was investigated at ambient conditions with Electrochemical Scanning Tunneling Microscopy (EC-STM). The atomically-thin Ag films were deposited on the Au(111) using Underpotential Deposition. The mere presence of a Ag monolayer drastically changed the amino acid/surface interactions despite the chemical similarity of Au and Ag. The adsorption of the AAs on the Ag monolayer drastically altered the surface and caused significant surface roughening distinct from 2D growth which had previously existed only on top of the surface. This roughening occurred layer-by-layer and was not restricted to the first layer of the surface as seen with sulfur containing molecules. Notably, this study demonstrates surface roughening that is occurring under extremely mild conditions highlighting the ability of Ag thin films to markedly alter surface chemistry in concert with biomolecules.

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 CO₂ and CH₄ 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 CO₂ or CH₄ 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 CO₂ or CH₄ into methanol. CeOx/Cu(111), Cu/CeOx/TiO₂(110) and Cu/TiC(001) exhibit an activity for the CO₂ → CH₃OH 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 CH₄.

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. Puntischer, 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 Fe₃O₄(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 H₂O) 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]

[1] Häussinger, Lohmüller, Watson, *Hydrogen, 2. Production*. In: Ullmann's Encyclopedia of Industrial Chemistry, 2011

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

[3] Bliem, Pavelec, Gamba, McDermott, Wang, Gerhold, Wagner, Osiecki, Schulte, Schmid, Blaha, Diebold, Parkinson, *Phys. Rev. B* **92**, p. 075440 (2015)

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 (CO₂) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO₂ 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 stuck to clean Rh(111), (2x1)-O/Rh(111), and (2x1)-O + RhO₂/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 CO₂ 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 CO₂ dissociation, 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.

[1] P. Auburger, I. Kemeny, C. Bertram, M. Lingges, M. Bockstedte, U. Bovensiepen, K. Morgenstern, *Phys. Rev. Lett.* **121**, 206001 (2018)

[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 CO₂ to ethanol in the presence of Cu [1] and N₂ 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

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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 nanopike topography which contributes to the electrochemical activity.

Contamination of the spiked surface raises the work function above that of the clean nanopikes. 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 nanopikes. 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.

[1] Y. Song, et al., *Chemistry Select* 1 (19), 6055 (2016).

[2] Y. Song, et al., *Sci. Adv.* 4(4)(2018).

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 mechanistic 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 mechanistic insight into the promoting effect of alloying. The trained GBR model outperforms the conventional derivative-based methods in terms of both predictability and mechanistic 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.

[2] R. Endo, T. Ohnishi, K. Takada, and T. Masuda, *J. Phys. Chem. Lett.* 2020, 11, 6649–6654.

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. Chukwunye*, *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. $\text{N}_2/\text{H}_2\text{O}$ 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 $\sim 3:1$, 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 $\sim 50\%$ at 10^{-9}

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¹ Torr N₂ partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N₂-surface binding in the absence of N₂ overpressure are consistent with N₂ binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N₂/H₂O 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 N₂ bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N₂ pi* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N₂ -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:

This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility, under Contract

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 CO₂ 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 200-300°C, 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 200°C. A thin Cu film was deposited onto a Si₃N₄ 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.

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 SiCl₄ 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 SiO₂ 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 SiO₂ without forming on a Si etching area by using a SiCl₄/H₂/Cl₂ 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 SiO₂ 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 SiO₂ mask, the layer was oxidized using an O₂ plasma treatment to improve the etching resistance during the Si-etching. The O₂ 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 SiO₂ 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 Y₂O₃ 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 Y₂O₃ [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 Y₂O₃ 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 Y₂O₃ [3]. We speculated that such tendency was caused by higher atomic number density of Y-O-F than that of Y₂O₃. Thus, the etching behavior of Y-O-F and Y₂O₃ 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 Y₂O₃ 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 Y₂O₃ was smaller than that of Y-O-F, suggesting that surface

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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. Hermans, 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 $Ar/CF_4/O_2$ remote 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_2 etching 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 chemical 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-H₂ 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.

[1] Zheng, L., Ling, L., Hua, X., Oehrlein, G. S. & Hudson, E. A. Studies of film deposition in fluorocarbon plasmas employing a small gap structure. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* 23, 634–642 (2005).

[2] Knoll, A. J., Pranda, A., Lee, H. & Oehrlein, G. S. Substrate temperature effect on migration behavior of fluorocarbon film precursors in high-aspect ratio structures. *J. Vac. Sci. Technol. B.* 37, 031802 (2019).

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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 SiO₂. 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 in gate-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 CF₄- and NF₃-based process chemistries to etch low-k materials including SiCN, SiOCN, and SiBCN along with reference materials including Si, SiO₂, 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 H₂ plasma operating at low temperature (50-200 °C) 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 H₂ and D₂ 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 10²⁰ m² s⁻¹. On the other hand, plain α -Fe foils showed very stable, but lower (10¹⁹ m² 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 H₂O, H₂, and O₂. 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 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 H₂ 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 H₂ at higher surface temperatures (\geq 600 K) reduces the TM silicate. Also, water dissociates readily on the metal silicate surfaces at 300 K. With an increase in H₂O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 mbar H₂O, molecular and dissociated water coexist (hydrogen bond OH/H₂O). 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 H₂-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 to be far more active than the majority sites exposed on basal

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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. MoS₂ nanocrystals are active catalysts in heteroatom extrusion from hydrocarbons (O, N, S) in oil and bio-oil processing (hydrotreating). Atom-resolved STM studies of MoS₂ nanocrystals as a supported model catalysts was used in combination with DFT analysis of molecule adsorption on MoS₂ 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 MoS₂ 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* O₂ 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* O₂ intercalation was executed by exposure to near-ambient partial pressures of O₂ (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 Cu₂O-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 Cu₂O-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 MoS₂, Blake Birmingham, Baylor University

MoS₂ 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 MoS₂ 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 MoS₂ catalyst during HER were monitored in-situ by electrochemical scanning tunneling microscopy (EC-STM). The nanoscale structure of the MoS₂ is correlated with its electrochemical activity in 0.5 M H₂SO₄(aq) electrolyte. Defects on the MoS₂ 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 MoS₂ 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. Benjamin 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

Surface Science Division

Room Ballroom A - Session SS-TuP

Surface Science Poster Session

SS-TuP-1 Monolayer Functionalization of Semiconductor and Metal Oxide Surfaces with Boron-Containing Precursors, *Dhamelyz Silva Quinones, C. Byron, A. Teplyakov*, University of Delaware

The monolayer functionalization reactions of Si (100) single crystal with boron-containing compounds, including boron trichloride, boric acid, and 4-fluorophenylboronic acid were studied in order to understand the interactions of these molecules with hydrogen and chlorine terminated-Si (100) for designing possible silicon doping processes. This study was compared with the surface modification of TiO₂ and Al₂O₃ nanoparticles with 4-fluorophenylboronic acid in solution in order to understand the attachment chemistry and to develop spectroscopic labels for surface characterization.

The modification chemistry was followed by X-ray photoelectron spectroscopy (XPS), solid-state NMR (ss-NMR), and infrared spectroscopy to determine the binding modes of the attached compound. Density functional theory was utilized to supplement the analysis, interpret the results of spectroscopic measurements, and to interrogate the surface stability of possible surface species.

The results obtained in these studies confirm the attachment of the boron trichloride, boric acid, and 4-fluorophenylboronic acid showing selectivity for the Cl-terminated Si (100) surface compared to H-terminated Si (100).

The attachment chemistry of 4-fluorophenylboronic acid on the TiO₂ and Al₂O₃ nanoparticles was confirmed with a high coverage and the type of attachment on each metal oxide surface is described.

This work provides fundamental understanding and a new pathway to obtain functionalized flat and nanoparticulate surfaces with boron-containing molecules. In the case of flat surfaces, these reactions can be used for selective-area monolayer doping or as a deposition resist. For oxide nanomaterials, the same approach can be used for spectroscopic labeling or for further functionalization.

SS-TuP-2 Detection of Chemically-induced Hot Electron Flux Amplified by Plasmonic Effect on Pt/Ag/TiO₂ Nanodiodes, *Mincheol Kang, B. Jeon, J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Concern about the energy resource crisis has encouraged study of the conversion and utilization of solar energy to improve catalytic efficiency, and the design of the surface plasmon-based photocatalyst is attracting particular attention as a competitive catalyst system. In this work, catalytic devices based on Schottky nanodiodes (Pt/Ag/TiO₂) were fabricated for antenna-reactor plasmonic photocatalysis; hot electrons generated during the chemical reaction can be directly detected through the diodes. In this system, the surface temperature was measured using thermovision to distinguish contributions of the plasmonic effect and the photothermal heating effect. When the light of the particular wavelength region is incident on the diodes, the flow of reaction-induced hot electrons (chemicurrent) and the catalytic activity (turnover frequency) are amplified by the plasmonic effect. Plasmonic photocatalytic performance can be controlled with light wavelengths, light intensity, surface temperature, and structures of nanodiodes. Also, the plasmonic effect is exhibited visually, using the finite difference time domain simulations. These results elucidate the hot electron flow on antenna-reactor photocatalysis and offer improved strategies for efficient catalytic devices.

SS-TuP-3 Boosting Hot Electron Generation and Catalytic Performance by Engineering Metal-Oxide Interfaces, *Kyoungjae Song, J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The interface between catalytic metal and oxide support is an important factor that affects reaction performance. However, metal-oxide and oxide-oxide interface studies have been limited, because of the complex structure of metal-oxide-oxide interface. To investigate the influence of the complex interfaces on both catalytic performance and hot electron flux, we used an inverse oxide-metal Schottky diode from CeO₂/Co₃O₄ nanocubes (NCs) on Pt film, which measures hot electron flux and reaction rate under an exothermic methanol oxidation reaction. Turnover frequency (TOF), partial oxidation selectivity, and hot electron flux were obtained on CeO₂/Co₃O₄ NCs on Pt film; TOF was higher by a factor of 2, selectivity to methyl

formate was higher by a factor of 1.5, and chemicurrent yield was higher by a factor of 7 compared to Co₃O₄ NCs on Pt film. Furthermore, the Co₃O₄ NCs half covered with CeO₂ showed higher values of both TOF and selectivity to methyl formate than CeO₂ NCs and Co₃O₄ NCs fully covered with CeO₂, indicating that the Co₃O₄/CeO₂ interface also affects the catalytic reaction. From ex situ XPS analysis, CeO₂-Co₃O₄ on Pt film showed the highest proportion of Ce³⁺ ions compared to both CeO₂ NCs and Co₃O₄ NCs fully covered with CeO₂ nanoparticles. The result indicate that CeO₂ can not only prevent the reduction of Co₃O₄ by supplying oxygen, but also boosts the methanol oxidation reaction by supplying oxygen to Pt film, leading to enhanced hot electron flux.

SS-TuP-4 Effect of Water Vapor on Oxidation Process of Cu(111) Surface and Sublayer; Ambient Pressure STM and XPS Studies, *Youngjae Kim, D. Kim, Y. Kim*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Y. Jeong*, Institute for Basic Science (IBS), Republic of Korea; *B. Jeong*, Korea Basic Science Institute (KBSI), Republic of Korea; *J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Copper-based materials are used for heterogeneous catalytic reactions, including CO oxidation, low-temperature water gas shift reactions, and CO₂ hydrogenation. These applications could benefit from a better understanding of the transitions between copper-based oxidation states, metallic Cu, Cu₂O, and CuO. In this work, we directly observed different oxidation processes on a Cu(111) single crystal, using ambient pressure scanning tunneling microscopy (AP-STM) and X-ray photoelectron spectroscopy (AP-XPS). The Cu(111) surface started to be oxidized at 0.01 Torr of pure O₂ under dry oxidation conditions. Time-lapse AP-STM and AP-XPS results showed that dry oxidation started at the step-edges in the form of adsorbed oxygen atoms, O_(ad), and progressed to the terrace in the Cu₂O phase. In addition, independent oxidations on the metallic Cu(111) terrace provided a more collapsed Cu₂O/Cu(111) surface structure. Under H₂O/O₂ mixed gas conditions, the humid oxidation of the Cu(111) surface occurred at 0.02 Torr. Time-lapse AP-STM images demonstrated that the oxidation also proceeded from the step-edges to the terrace, but there were no independent oxidations on the terrace, leading to fewer defect sites on the Cu₂O/Cu(111) surface. Time-lapse AP-XPS results showed that the appearances of O_(ad) and Cu₂O peaks were similar to dry oxidation. Hydroxides were observed after the surface was completely saturated by the Cu₂O phase. Furthermore, by analyzing the relative intensity and peak area of XP spectra, we found that the depth of Cu₂O differed dramatically in the dry and humid oxidation processes. The Cu₂O thickness of the dry oxidation was greater than that of the humid oxidation under all similar pressures. Water molecules from the humid oxidation caused a different oxidation mechanism from the dry oxidation, with a different degree of oxidation. Specifically, the water vapor molecules inhibited sublayer oxidations, inducing less coverage of the step-edges on the Cu(111) surface than under the dry oxidation conditions.

SS-TuP-5 Phase-Dependence on the Friction of Exfoliated MoX₂ (X:S, Te) Layers, *DooHo Lee*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *H. Jeong*, Korea Advanced Institute of Science and Technology, Republic of Korea; *H. Lee*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Y. Kim*, 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

Transition metal dichalcogenides (TMDs) 2-dimensional (2D) material is widely studied for its semiconducting nature, which makes it potentially suitable for applications in thin-film transistors.¹ Among TMDs, the molybdenum disulfide (MoS₂) monolayer is an atomically thin semiconductor with a bandgap of 1.8 eV. MoS₂ is also getting attention as an anode for Li-ion batteries, because of its Li intercalation mechanism. Electron donations from Li induce a MoS₂ phase transition from the stable semiconducting 2H phase to the metallic 1T phase. While MoS₂ chemically exfoliated with Li showed friction at a similar level with mica, mechanically exfoliated MoS₂ exhibits significantly lower friction than mica.²

We turned mechanically exfoliated 2H-MoS₂ into 1T-MoS₂ by a lithiation process and measured atomic-scale tribological and electrical properties of MoS₂, including friction, with atomic force microscopy (AFM). We report that the friction of MoS₂ increased significantly with the phase transition of 2H to 1T. The friction proportion of 2H-MoS₂ and 1T-MoS₂ is 0.12:1.07, with normalization to the value of mica. We also measured the friction of

molybdenum ditelluride (MoTe₂), of which the pure 1T phase is commercially available, since it shows a stable 1T phase as well as a 2H phase. The friction proportion of exfoliated 1T-MoTe₂ and 2H-MoTe₂ is 0.18:1.09, normalized with the friction of mica. With density functional theory (DFT) calculation, we attribute the higher friction of 1T-MoX₂ to the increased overlap of phonon density of states (DOS) with mica substrate, as well as the higher energy barrier in the potential energy surface of 1T-MoX₂. The study suggests the intriguing possibility of tuning friction by a phase transition of 2D materials.

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SS-TuP-6 Electron Dynamics at a Confined Cu_{2-x}O/Cu Interface, J. Trey Diulus, J. Beckord, Z. Novotny, N. Comini, M. Hengsberger, J. Osterwalder, University of Zurich, Switzerland

Cuprous oxide (Cu₂O) is a promising photocathode material for the hydrogen evolution reaction (HER) due to its bandgap in the visible spectrum, relative abundance, and low cost. However, Cu₂O is unstable in aqueous solutions. To increase the corrosion resistance, a chemically stable capping layer, such as hexagonal boron nitride (*h*-BN), can be deposited on the Cu₂O surface. While the growth of *h*-BN on top of non-metallic oxides by chemical vapor deposition is difficult, one approach is to oxidize a Cu metal substrate underneath an *h*-BN monolayer via O₂ intercalation. This preparation method was implemented by exposing a Cu(111) single crystal with an *h*-BN monolayer to partial pressures of O₂ up to the millibar range at temperatures up to 200 °C. The atomic structure was unraveled with a combination of surface science techniques at the Swiss Light Source. The *h*-BN layer remains intact and the Cu_{2-x}O oxide film has a thickness of a few atomic layers (3-4 Å) displaying structural motifs typical of the Cu₂O(111) surface, comprising a chemisorbed O layer and a Cu_{2-x}O-like trilayer positioned in between the *h*-BN and the substrate. A well-ordered *h*-BN/Cu_{2-x}O/Cu(111) sample was prepared for characterizing the electronic structure and electron dynamics with ultraviolet and pump-probe photoemission spectroscopy. Angle-resolved photoelectron spectroscopy (ARPES) after oxidation shows the sharp σ and π bands of an intact *h*-BN monolayer and another narrow state 1.2 eV below the Fermi level, attributed to the valence band of Cu₂O that is shifted downwards due to the contact to a metallic copper substrate. Time-resolved two-photon photoemission (tr-2PPE) spectra show a short-lived state at 1.0 eV and a long-lived state at 0.1 eV above the Fermi level. The state at about 1 eV has a strong parabolic dispersion matching the conduction band of Cu₂O, whereas the low energy state has no dispersion, pointing towards a localized defect state of the Cu_{2-x}O layer. Such defect states were also observed on the reconstructed bulk Cu₂O(111) surface and were attributed to charged oxygen vacancy states with very high capture coefficients for trapping conduction electrons. The visible conduction band is promising, but the trapping is detrimental to the function as efficient photocatalyst. To render this system into a viable photocathode, the oxide film should be grown to a thickness adapted to the light absorption length of about 30 nm, and the defect concentration should be further reduced.

SS-TuP-7 Understanding Interfaces to Develop Advanced Materials for Industrial Applications, Pierluigi Bilotto Bilotto, M. Ostermann, D. Miano, Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria; M. Valtiner, Centre for Electrochemistry and Surface Technology (CEST GmbH), Vienna University of Technology (TUW), Austria

Industries eager for innovative solutions to strike against the climate crisis. For instance, that translates into developing innovative composites material expressing multifunctionalities, reduce the energy produced because of wearing via green solid lubricant, or for instance optimizing yield and efficiency of industrial processes.

The poster will summarize the projects and results obtained at the Centre for Electrochemistry and Surface Technology (CEST, Austria) in the *material and interfaces* research areas for application in aeronautical, aviation and semiconductor industries. Specifically, we propose a clean and upscalable process for the production of graphene oxide,¹ which will be used for advanced coatings expressing de-icing, lightning strike protection and corrosion functionalities. Moreover, for the *interface* area we will show our strategies to elucidate the tribological mechanisms of MXenes based solid lubricant, and the utilization of nanobubbles to optimize wafer cleaning processes.

(1) Ostermann M. *et al* – (submitted in May 2022)

SS-TuP-8 Investigation of CO Oxidation on Rh(111) with IRRAS, Faith Lewis, D. Killelea, Loyola University Chicago

Fourier-transform Infrared (FTIR) spectroscopy is widely applied to identify smaller molecules adsorbed to metal surfaces. Here, FTIR was coupled to an ultra-high vacuum (UHV) system where the sample environment was carefully controlled to eliminate interference from atmospheric species. IR reflection measurements from a metal surface were performed under UHV conditions and the catalytic oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) over Rh(111) was investigated. This reaction was used as a probe reaction to determine the relative reactivity of various oxidic species. We determined the binding sites on different oxygenaceous phase and determined their chemical significance towards heterogeneously catalyzed oxidation of CO. This provided atomic level information regarding oxidation reactions, and advanced our understanding of the different surface phases relevant to many Rh catalyzed processes.

SS-TuP-9 Modifications of Surface Optoelectronics in ZnO Nano- and Microcrystals Following Exposure to *Staphylococcus Aureus* and Bacterial Growth Media, Dustin Johnson, Texas Christian University; J. Reeks, INSTITUTE OF LOW TEMPERATURE AND STRUCTURE RESEARCH - POLISH ACADEMY OF SCIENCES, Poland; A. Caron, Texas Christian University; I. Tzoka, University of Texas at Arlington; O. Castillo, K. Nguyen, Paschal High School; M. Hattarki, Rice University; S. McGillivray, Y. Strzhemechny, Texas Christian University

A combination of useful optoelectronic properties and high biocompatibility rendered ZnO a versatile material with budding applications at the nano- and microscale, among which are pharmaceuticals, bioengineering and medical diagnostics, specifically employing ZnO as an antibacterial agent. With bacterial growth inhibition observed for both gram-positive and gram-negative bacteria as well as antibiotic strains, the antimicrobial action of ZnO is both promising and well documented. Yet application is significantly hindered due to uncertainty regarding fundamental mechanisms underlying such properties. Presently, discussion centers on several proposed mechanisms, such as generation of various reactive oxygen species, Zn ion release and surface-surface interactions between the bacterial cell wall and free crystalline surface. Here we investigate surface and near-surface modifications of optoelectronic properties in ZnO microcrystals following exposure to bacterial environments to elucidate those specific mechanisms. Microscale ZnO crystals are well-suited to serve as a platform to investigate the role played by crystalline surfaces as they exhibit comparable antibacterial action to nanoscale forms while minimizing effects of internalization. A bottom-up hydrothermal growth method allows for controlled synthesis of high-quality ZnO microcrystals with tunable morphology and controllable relative abundance of polar vs. non-polar surfaces. The quality of crystalline lattice and free surface as well as the predominant morphology of these samples are confirmed by FE-SEM, EDXS, and surface photovoltage (SPV) studies. The antimicrobial efficacy of these particles is characterized by minimum inhibitory concentration assays, utilizing wild type *s. aureus* in Mueller Hinton broth media. A series of optoelectronic experiments including temperature-dependent PL spectroscopy as well as spectroscopic and transient SPV are performed to probe changes occurring at ZnO surfaces during such assays. These comparative studies reveal that antibacterial action of ZnO microparticles is primarily rooted in interactions between crystalline surfaces and extracellular material of the bacteria. This is supported by observed degradation of the crystal surface and significant spectral changes due to surface interactions with bacteria and growth media. We show that interaction with *s. aureus* results in considerable change to the excitonic structure of the ZnO microcrystals. We also demonstrate dependence of such interactions on growth media, specifically those containing aqueous phosphates, finding not only changes in bactericidal efficacy but also the nature of these interactions.

SS-TuP-10 A Potential Model for Investigating the Edge Properties of FeO by Taking Advantage of Different Metal Affinities, Dairong Liu, L. Li, S. Mahapatra, N. Jiang, University of Illinois - Chicago

As a series of catalysts with wide catalysis applications and high economic efficiency, iron oxide has caught extensive attraction in the past several decades. During the various types of iron oxide, the FeO, well known as Ferrous oxide, has been proved to have high catalysis reactivities in catalysis reaction, e.g. CO catalysis oxidation. To obtain a throughout understanding of the catalysis mechanism, it is vital to investigate the surface and edge properties of FeO. In the past decade, various techniques have been applied to reach the surface properties of FeO, the researchers found that the edge of FeO plays an important role in the initial CO oxidation. However, due to the limit of the characteristic technique, the

specific edge properties of FeO are still under debate. Here, we established a model, to selectively expose the distinguished type of edges on FeO. By taking advantage of the different metal affinities of the O-edge and Fe-edge in FeO, the Pd and Pt are introduced and found to selectively block the distinguished edge. The blocked edges are expected to be excluded from the catalysis reaction, which means that in the reaction, only the unblocked type of edge will be involved. By further comparison of the different performances of Fe-edge and O-edge selective exposed samples, the roles of different types of edge in the catalysis reaction can be studied, which can give an insight into the edge properties of the FeO and contribute to the design of high-efficiency FeO catalyst.

SS-TuP-11 Effects of Thermal Atomic Layer Etching on the Magnetic Properties of CoFeB, Marissa Pina, M. Konh, Y. Wang, J. Xiao, A. Tepyakov, University of Delaware

Atomic layer etching (ALE) is emerging as a major approach to control feature size of modern devices at the atomic scale. Thermal approaches are especially important for expanding the capabilities into the 3rd dimension and approaching more-than-Moore technology. However, for complex materials that are used in spintronics and magnonics, developing thermal ALE methods is difficult because the materials often contain several elements, some of the elements have not been investigated for ALE, little control over the surface properties of the resulting films is established, and their effect on the physical properties of the device (such as magnetic properties) has not been investigated. This work will interrogate the chemistry of thermal ALE of CoFeB alloys used in the magnetic tunnel junction and present an investigation of the effect of this chemistry on the magnetic properties of thin films. The effect of a half-cycle of chlorination and a full cycle of exposure to chlorine and acetyl acetone will be compared for films of comparable thickness produced by multiple ALE cycles and by ion milling. The effect of chemistry and surface smoothing will be evaluated based on a comparison of surface characterization by atomic force microscopy and XPS with the outcomes of ferromagnetic resonance measurements. Further pathways for controlling the effects of ALE on the physical properties of thin films prepared from different materials will be proposed.

SS-TuP-12 The Diamond (111) Surface Reconstruction and Epitaxial Graphene Interface, Benjamin Reed, National Physical Laboratory, UK; M. Bathen, ETH Zurich, Switzerland; J. Ash, Aberystwyth University, UK; C. Meara, Newcastle University, UK; A. Zakharov, Max IV Laboratory, Sweden; J. Goss, Newcastle University, UK; J. Wells, University of Oslo, Norway; D. Evans, Aberystwyth University, UK; S. Cooil, University of Oslo, Norway

There is rejuvenated interest in (111)-orientated diamond as a state-of-the-art electronic material, especially for quantum information and sensing applications, and its nanoscale properties for the production of diamond-graphene interfaces. However fundamental studies of the diamond (111) surface remain incomplete and there is an unresolved controversy surrounding the electronic nature of the C(111)-(2×1) surface. Density functional theory (DFT) calculations predict symmetrically π -bonded surface chains that exhibit a metallic surface state that intersects the Fermi level (E_F),^{1,2} but experimental angle-resolved photoemission spectroscopy (ARPES) studies have shown a semiconducting surface ($\Delta E = 0.5$ eV) that corresponds to a dimerized π -bonded surface chain model.^{3,4}

Our combined ARPES and DFT results show that the C(111)-(2×1) surface is metallic as it has electronic states that intersect E_F . This is in strong agreement with a symmetrically π -bonded chain model and should contribute to resolving the controversies that exist in the literature surrounding the electronic nature of this surface. Above 1000°C in vacuo, the reconstructed surface atoms are liberated into a free-standing monolayer of epitaxial graphene which exists above a newly formed C(111)-(2×1) surface and appears to have little substrate interaction as the Dirac-point is observed at E_F . We also demonstrate that is possible to hydrogen terminate the underlying diamond surface by means of plasma processing without removing the graphene layer, forming a graphene-semiconductor interface.⁵

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SS-TuP-13 The Nature of Electrical Double Layer Near Graphene and Anatase, Xiao Zhao, S. Yang, M. Salmeron, LBNL

Structure and profiles of electrical double layer (EDL) govern many electrochemical reactions. Fundamental knowledge of EDL is based on simplified Gouy-Chapman and Stern model, in which solvation and specific interactions of the electrolyte ions with the electrode are neglected. Here we present our recent progress determining the EDL structure near substrate-free graphene and near thin anatase films using Raman, Sum Frequency Vibrational Spectroscopy (SFVS), Kelvin Probe Force Microscopy (KPFM) and Near Edge X-ray Absorption Fine Spectroscopy (NEXAFS). Near suspended graphene SO_4^{2-} anions were found to preferentially accumulate near the interface at open circuit potential (OCP), creating an electrical field that orients water molecules below the interface while no such increase was observed with Cl⁻. The degree of orientation of the water molecules as well as the electrical double layer strength increased further when positive voltages are applied. Negative voltages on the other hand produce smaller changes in the intensity of the H-bonded water peaks, but affect the intensity and frequency of the dangling O-H bond peaks. Near anatase ice-like water layer has been observed using SFVS and NEXAFS, and different segregation behavior has been observed for Na⁺ and Cl⁻ under both OCP and applied bias. Our findings demonstrate the effect of solvation and electrode-ion interactions on EDL structure and call for theoretical insight in this direction.

SS-TuP-14 Reactions of Tetrakis(Dimethylamido)Titanium on Halogenated, Hydrogenated, and Oxidized Silicon Monolayer Resists for Atomic Layer Deposition, Tyler Parke, D. Silva-Quinones, A. Tepyakov, University of Delaware

In atomic layer deposition (ALD) of TiO₂ with titanium tetrachloride (TiCl₄) and water, silicon (100) substrates with atomic chlorine (Cl-Si) or hydrogen (H-Si) terminations have previously been shown to be non-growth surfaces, resisting adsorption of and reaction with TiCl₄, as opposed to reactive oxidized silicon (HO-Si) growth surfaces, upon which TiCl₄ readily deposits. However, Cl-Si(100) degrades and loses selectivity rapidly under ALD conditions, leading to TiCl₄ nucleation on oxidized surface sites. In contrast, tetrakis(dimethylamido)titanium (TDMAT) follows a different reaction pathway on Si(100) surfaces, implying a difference in TDMAT's surface selectivity on silicon terminated with chlorine or perhaps other halogens, as well as a difference in the mechanism and extent of the selectivity loss. Here, the reactivity of TDMAT was studied under ALD conditions with oxidized, halogenated, and hydrogenated Si(100) surfaces. TiO₂ deposition was monitored on each surface using *ex situ* X-ray photoelectron spectroscopy (XPS). The initial nucleation behavior in the first few ALD cycles was compared between each surface using atomic force microscopy (AFM). Details of the bonding of TDMAT to the surface were elucidated using spectroscopic data in conjunction with density functional theory (DFT) observables on models of local surface geometry to propose surface reaction pathways.

SS-TuP-15 A 2D Bismuth-induced Honeycomb Surface Structure on GaAs(111), Yi Liu, S. Benter, Lund University, Sweden; C. Ong, R. Maciel, O. Eriksson, Uppsala University, Sweden; A. Mikkelsen, R. Timm, Lund University, Sweden

Bi-containing III-V semiconductors are of significant interest due to their superior charge carrier mobility, tunable direct band gap, large spin-orbit splitting, and predicted non-trivial topological behavior. This is relevant for realizing quantum information technology due to a large flexibility in material combinations and a potential for room-temperature operation. However, the realization of ordered, crystalline alloys with high Bi content remains a challenge. Epitaxial growth of III-V films only allowed dilute compounds with very low Bi atom incorporation, while surface evaporation has typically demonstrated Bi metallic films on top of the semiconductor surfaces. Instead, formation of ordered 2D semiconducting III-V:Bi films remains a desired alternative.

Here, we present the successful Bi incorporation into a clean GaAs(111)B surface, based on Bi deposition under optimized growth conditions. Atomically resolved low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S) shows a well-ordered large-scale honeycomb structure, consisting of Bi atoms in a $\sqrt{3}\times\sqrt{3}$ 30° reconstruction on GaAs(111). An almost defect-free, large-scale honeycomb structure is obtained after short anneal. X-ray photoelectron spectroscopy proves the successful incorporation of Bi atoms in the GaAs surface and shows that

the Bi atoms of the honeycomb structure only bond to the underlying As atoms. This is supported by density functional theory calculations which confirm the honeycomb structure, including a preferential formation of Bi-As bonds, and predict Bi-induced electronic bands within the GaAs band gap that open up a gap of non-trivial topological nature. STS results support the existence of Bi-induced states within the GaAs band gap.

The ordered Bi-induced 2D layer with a high Bi content of up to 67% surface coverage, covalently bonded to the GaAs substrate, and indications for non-trivial topological behavior is a great step towards realizing III-V semiconductor heterostructures with high Bi content that make use of the large spin-orbit coupling of Bi for enabling novel electronic properties. Furthermore, this result is a successful example for Bi-introduced low-dimensional structures with unique electronic states in III-V semiconductor systems.

SS-TuP-16 Hydrochloride Production from Dichlorosilane Decomposition and Its Impact on Atomic Layer Deposition of Silicon Nitride, *Tsung-Hsuan Yang, E. Cheng, G. Hwang, S. Johnson, J. Ekerdt*, University of Texas at Austin; *P. Ventzek, T. Iwao, J. Zhao*, Tokyo Electron America Inc.; *K. Ishibashi*, Tokyo Electron Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for the controlled growth of silicon nitride (SiN) thin films. The advantages of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures. In this talk, we will present molecular mechanisms underlying the PEALD of SiN thin films using dichlorosilane (DCS) as the Si source and N_2/NH_3 plasma as the N source. The adsorption and decomposition of DCS have been found to be sensitive to the surface functional groups; especially, the presence of primary amines plays a critical role in the silicon deposition half cycle. According to our recent studies, the by-products of DCS decomposition, H^+/Cl^- pairs, may have a significant effect on the film quality and deposition temperature. First-principles calculations predict that H^+/Cl^- pairs are strongly bound to the H-terminated N-rich surface by forming $-NH_3^+/Cl^-$ ionic complexes. Because of the sizable binding energy (~ 1 eV), it would be difficult to remove H^+/Cl^- pairs from the surface unless the PEALD temperature is substantially high. This implies that the reaction of DCS with surface primary amines, and in turn SiN ALD, can be significantly suppressed by the presence of H^+/Cl^- pairs at relatively low temperatures. The existence of H^+/Cl^- has been confirmed by FTIR measurements which shows two distinctive peaks at 1420 and 2800 cm^{-1} .

SS-TuP-18 Enhancing Fiber-Coupled Thermal Emission Collection Using IR Plasmonic Coating, *Aman Patel, R. Kayastha, K. Agyepong, B. Birmingham, Z. Zhang*, Baylor University

Current thermal emission measurement devices have made significant strides in the past few decades but with the current progress of technology towards smaller scale systems, the spatial resolution capabilities of current devices have become inadequate as they utilize the far field emission. The near field emission has orders of magnitude larger signal intensity compared to the far field emission. Current techniques like near field scanning optical microscopy (NSOM) collect the near field emission to improve spatial resolution but remain susceptible to low signal-to-noise ratio. In this experiment, we use titanium nitride (TiN) as an IR-plasmonic coating to enhance the near-field thermal emission collection. Optical fibers were etched to produce different tip geometries, coated with TiN using directed thermal vapor deposition, and put into a furnace to conduct thermal measurements at various temperatures. The collected thermal emissions using the fiber probes before and after TiN coating were compared to analyze the collection of the near field emission. The performance of the plasmonic TiN thin film was compared with a traditional plasmonic metal Au, at temperatures below 600°C. An increase in signal intensity of the collected thermal emission was observed for fiber tips coated with TiN and with Au. Probes with different TiN coating thicknesses and different tip geometries have been tested to develop a thermal probe with an improved signal-to-noise ratio. The thermal probe is integrated into an NSOM setup, for nanoscale thermal measurements for samples.

SS-TuP-19 The Effects of Surface Treatments on the Nucleation and Growth of Ruthenium on Tantalum Nitride, *C. Feit, U. Kumar, N. Berriel, Luis Tomar, S. Seal, P. Banerjee*, University of Central Florida

Ruthenium (Ru) has emerged as an alternative to copper interconnects acting as a diffusion barrier, leading to improved electromigration. Atomic layer deposition is widely used for high-quality, ultra-thin film deposition. However, the deposition of ultra-thin Ru films is challenging. Current Ru ALD processes exhibit island-like grow and long nucleation delays, driven

by the surface reactions among sterically bulky precursors, oxidation state of the metal center, and wettability of the substrate. Due to poor nucleation of ruthenium on industrially relevant tantalum nitride (TaN) surfaces, surface engineering is required to reduce Ru liners to competitive widths.

This work examines the effects Ru nucleation and growth, using ruthenium dimethyl butadiene tri-carbonyl (Ru(DMBD)(CO)₃) and H₂O on ultra-violet ozone treatment of TaN. The film nucleation and surface roughness is measured using atomic force microscopy (AFM). The Ru film thickness is measured by spectroscopic ellipsometry. The surface chemistry is investigated using X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Furthermore, the thermal conductance and electrical conductance confirm enhance film coalescence. Continuous Ru films can be achieved at ~ 2 nm on UV-ozone treated TaN compared to ~ 5 nm on untreated TaN.

SS-TuP-20 Laser Assisted Thermal Reactivity of Alkanes on Pt(111), *Julissa Velasquez*, University of Virginia

A molecular-level understanding of heterogeneous reactions on catalytic surfaces remains to be achieved leading to limitations in improved catalyst design. Alkane dissociative chemisorption on transition metal catalyst surfaces (e.g. Pt, Rh, Cu, etc.) is a key elementary step in alkane reforming providing an important model system to understand surface reaction kinetics and dynamics. The reactivity of a gas phase molecule striking a surface can be described by the molecule's Dissociative Sticking Coefficient (DSC). A DSC describes the probability of a molecule to dissociate on a surface $[RH_{(g)} \leftrightarrow R_{(c)}+H_{(c)}]$. DSCs can be resolved in detail by specifications of temperature (T), energy (E_t , E_v , E_r), and angle (θ) of the incident molecules providing enhanced details about the system's kinetics and dynamics. In some instances, DSCs are too small ($<10^{-6}$) to measure by conventional elemental analysis (Auger Electron Spectroscopy). Instead, it is desirable to study the reactions that produce alkanes in the reverse direction, $[R_{(c)}+H_{(c)} \leftrightarrow RH_{(g)}]$. Laser-assisted thermal associative desorption/Laser activated dissociative desorption (LAAD/LADD) using a 10ns pulsed laser allows for the measurement of the alkane product time-of-flight spectra to a quadrupole mass spectrometer.^{1,2} The translational energy distribution, $Pt(E_t)$, of the desorbing alkanes should be identical to the energy distribution of the successfully reacting alkane molecules in the reverse reaction, at the reaction temperature, via the principle of detailed balance.

Implementing this experimental technique required an understanding of the laser's interaction with a Pt single crystal surface. Theoretical laser induced surface temperature jump calculations were used to predict the surface temperature (T_s) rise caused by the laser at a specific pulse energy and beam size.³ For a thermal reaction, with an Arrhenius rate constant, under fast laser heating a majority of reactivity occurs at the peak surface temperature such that a quasi-isothermal reactivity at the peak temperature (T_s) is achieved. Theoretical work from the Harrison Group has successfully simulated LAAD experiments for $[CH_{3(c)}+H_{(c)} \leftrightarrow CH_{4(g)}]$ on Pt(111)⁴ and Ru(0001)². Here we present experimental limits for Nd:YAG laser to avoid surface damage or induce alteration to the desorbing flux. The first implementation of the LAAD/LADD experimental technique in our lab has been to look at the laser assisted thermal desorption of methane $[CH_{4(ad)} \rightarrow CH_{4(g)}]$ by measuring the methane $Pt(E_t)$, which is expected to roughly be a flux-weighted Maxwell-Boltzmann distribution at the desorption temperature.

SS-TuP-21 ID31 - High-Energy Beamline at ESRF for Buried Interface Structure and Materials Processing, *Andrea Sartori, J. Drnec*, ESRF, France

Complex heterogeneous materials, and their interfaces, inside operating devices can only be studied adequately by combining experimental methods to reveal the interplay between the microscopic material/interface properties and the macroscopic device performances. The need for combining techniques is instrumental in the development of hard x-ray synchrotron methods applied in situ and operando for studying both real devices under operating conditions and idealized model systems under precisely controlled environments. The high energy beamline ID31 of ESRF, dedicated for studies of buried surfaces and interfaces, enables a portfolio of hard x-ray characterization techniques, including reflectivity, wide angle diffraction both in

transmission and grazing incidence geometry, small angle x-ray scattering, and imaging methods coupled with great versatility in choosing beam sizes (minimum: horizontal 20.0 x vertical 3.0 μm^2 , maximum horizontal: 2.0 x vertical 1.0 mm^2), energy range (21.0 – 150 keV) and detectors optimized for high energy x-rays. The design enables many different studies with remarkable potential. More details about the beamline are reported in the supplemental file.

In this contribution we will discuss the design and the capability of the beamline, together with example of in situ experiment in the field of liquid organic hydrogen carrier (LOHC). By using high energy X-Ray diffraction to study the dehydrogenation reaction of benzyltoluene. We investigated, at atomic resolution, a catalyst of single crystal Al_2O_3 sample supporting Pt nanoparticles. The experiments were performed in a custom-made reactor in operando under realistic conditions (260 °C, 1.5 bar). The first results show an increase of the full width half maximum and the shift of the Pt (111) peak suggesting possible formation of a carbide in the nanoparticles surface, extended more than just one monolayer. Further characterization and experiments are in progress.

SS-TuP-22 Modeling Surface Interactions: Methods and Select Applications, *Sierra Jubin*, Princeton University; *Y. Barsukov*, Princeton Plasma Physics Laboratory; *I. Kaganovich*, Princeton Plasma Physics Laboratory

Though molecular dynamics (MD) is a powerful tool for investigating materials properties, one must take great care that the MD potentials properly represent the system of interest. The modeling of surface interactions presents a particularly difficult challenge. MD potentials which reproduce bulk properties may fail to predict energies and geometries related to the adsorption and reaction of atoms and molecules on the surface. For example, our MD simulations showed that bond order MD potentials which have been used to describe amorphous boronized graphite yield highly unrealistic models of boron adsorption on a graphene sheet [1].

For systems where suitable MD potentials are not available or lead to questionable results, the DFTB MD (density functional tight binding molecular dynamics) method might be used. Note that DFTB is a semi-empirical parameterized method, and parameter sets exist for a limited number of chemical systems. Moreover, there is no guarantee that DFTB parameters for a set of elements give the correct structures of all possible compounds consisting of this set of elements. For example, available DFTB parameter sets can describe the geometry of stable NH_3 and HF molecules, but do not predict the existence of salts with an ammonium cation, such as NH_4^+F^- and $\text{NH}_4^+\text{HF}_2^-$. For such complex systems, the Car-Parrinello MD method can be used rather than DFTB. Another issue with MD methods can occur in chemical reactions proceeding via a significant barrier, because the simulation time required to overcome the barrier may be prohibitively long. Nonetheless, our group has used DFTB MD to successfully explore the formation of BN chains and fulborenes by self-assembly [2].

A powerful method for the study of chemical reactions with large energy barriers is the use of DFT (density functional theory) in conjunction with transition state theory, which can predict the probabilities of elementary steps in surface reactions. Often, the rate of a whole reaction is limited by the rate of the slowest elementary step within that reaction. For example, using DFT modeling we showed that F_2 dissociative adsorption on a fluorinated Si surface leads to Si-Si bond breaking, following a reaction pathway that proceeds over a barrier. Thus, the rate of Si etching by F_2 can be calculated as a function of F_2 partial pressure and temperature. This modeling also demonstrated that the rates of F_2 dissociative adsorption on (111), (110) and (100) oriented Si surfaces are significantly different at room temperature.

[1] S Jubin *et al* 2022 *Frontiers in Physics* **10** DOI: 10.3389/fphy.2022.908694

[2] Y Barsukov *et al* 2021 *Nanotechnology* **32** 475604 DOI: 10.1088/1361-6528/ac1c20

SS-TuP-24 Deterministic Switching Using Unconventional Spin-Orbit Torques in Atomically Clean WTe_2 /FGT Heterostructures, *Sean Yuan*, *I. Kao*, *R. Muzzio*, Carnegie Mellon University; *J. Edgar*, Kansas State University; *J. Goldberger*, Ohio State University; *J. Yan*, Oak Ridge National Laboratory; *J. Hwang*, Ohio State University; *J. Katoch*, *S. Singh*, Carnegie Mellon University

Layered materials with low-symmetry crystal structure, such as WTe_2 and MoTe_2 , are energy efficient spin source materials for spintronics-based memory and logic devices. We will present results showing the fabrication of spin-orbit torque (SOT) switching devices constructed out of vdW based heterostructures with atomically clean interfaces. The sharpness of the

interface is essential to suppress interfacial spin dephasing, and thus enhance SOT efficiency for spintronics applications. Here, we present results showing the fabrication of SOT switching devices with atomically sharp interfaces, which we construct to enable SOT-driven deterministic control of a magnet with out-of-plane polarization¹. This is challenging because deterministic field-free switching of a perpendicularly polarized ferromagnet requires an out-of-plane anti-damping torque, which is typically prohibited due to in-plane crystal symmetries within conventional spin sources. In order to achieve this unconventional SOT form, we exploit the low in-plane crystal symmetries of WTe_2 , enabling an out-of-plane SOT component^{2,3}. This work is the first step towards realizing all-vdW based spintronic devices that are ultra-thin and have ultra-low power consumption for their operation.

1. Kao, I.H., *et al.*, *Nat. Mater.* **21**, 1029–1034 (2022).

2. D. MacNeill *et al.*, *Nat. Phys.* **13**, 300 (2017)

3. F. Xue *et al.*, *Phys. Rev. B* **102**, 01440 (2020)

SS-TuP-25 Preparing and Characterizing Thin Hexagonal Boron Nitride Flakes for Creating Spin Defects, *Seth Eisenberger*, *I. Kao*, *R. Muzzio*, *J. Katoch*, *S. Singh*, Carnegie Mellon University

Spin defects in layered van der Waals systems, such as hexagonal boron nitride (h-BN), is an appealing platform for quantum sensing. In this work, we will discuss the preparation and characterization of atomically thin flakes of h-BN using different experimental methods including Raman spectroscopy and atomic force microscopy. We have successfully coupled h-BN flakes to on-chip micro coplanar waveguides and have created atomic defects in h-BN using high energy ion implantation. We will also discuss methods for transferring h-BN flakes onto scanning transmission electron microscopy grids for characterizing these defects.

SS-TuP-26 Visualizing the Electronic Structure of Multiple Twisted Bilayer Graphene Domains, *Indra Periwal*, *R. Muzzio*, Carnegie Mellon University; *C. Jozwiak*, *A. Bostwick*, *E. Rotenberg*, Lawrence Berkeley National Laboratory; *S. Singh*, *J. Katoch*, Carnegie Mellon University

Twisted two dimensional (2D) heterostructures have emerged as a novel way to modulate the physical properties of matter, the most famous of which is the unconventional superconductivity in twisted bilayer graphene (twBG). It is therefore essential to determine the evolution of twisted bilayers as we vary the twist angle. In this study, we employ nano-focused angle resolved photoemission spectroscopy (ARPES) to investigate twBG over a wide range of twist angles. We will discuss the heterostructure fabrication, momentum-resolved measurement, and 4-dimensional analysis of our sample which contains various twBG domains. Each domain contains a different twist angle and we will discuss the implications of the change in the electronic structure.

SS-TuP-27 Angle-Resolved XPS Analysis of the Oxidation of Ru Thin Films, *Shivan Antar*, *A. Valenti*, *R. Wheeler*, *C. Ventrice*, SUNY Polytechnic Institute; *M. Strohmayer*, *J. Brewer*, *C. Nassar*, *C. Keimel*, Menlo Micro

Ruthenium is often used as an electrical contact material because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide under ambient conditions is RuO_2 , which is an electrically conductive oxide. The goal of this study is to determine the stoichiometry and measured thickness of the surface oxide on Ru formed by various and typical semiconductor fabrication processing techniques such as reactive ion etch, plasma ashing processes, silicon dioxide depositions, and annealing in various environments. The primary analysis technique used for this study is X-ray photoelectron spectroscopy (XPS). The Ru thin films were deposited on $\text{SiO}_2/\text{Si}(100)$ substrates. Angle-resolved XPS data were collected at takeoff angles of 10°, 20°, 30°, 40°, 50°, and 60°, where the takeoff angle is measured from the plane of the surface. The acceptance angle of each of the angle-resolved measurements was 10°. Angle-integrated XPS data were collected at a takeoff angle of 45° and acceptance angle of 40°. Analysis of the Ru-3d XPS spectrum of the as-grown Ru film indicates that the native oxide is in a 2+ state and is less than a nm thick. Annealing at atmospheric pressure results in the formation of Ru in a 4+ state (RuO_2) at the surface that is ~2 nm thick. In addition, the presence of higher order oxides and surface carbon is detected after the anneal. Performing either a RIE or ash process on the as-deposited Ru film also results in the formation of RuO_2 but with a thickness of ~1 nm. Higher order oxides (RuO_x) and carbon are also present in the surface region after these processing techniques have been performed but at a lower surface concentration than the sample annealed in air. Analysis of the O-1s XPS

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spectra of the samples indicates the presence of an ~1 nm thick water layer on top of each sample during the measurements.

This project is funded in part by the New York State Center for Advanced Technology in Nanomaterials and Nanoelectronics (CATN2).

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 \rightarrow Provide information about the contact area
2. Force data \rightarrow Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) \rightarrow 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

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that a generally uniform layer was formed on the surface and this ASEI is roughly $200 \mu\text{m}$ 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 ($\sim 10\text{nm}$) 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

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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 (SEI), 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 K α and Cr K α 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 μ m 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 component 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 -Al₂O₃ present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of Cs_x(CH₃NH₃)_{1-x}PbBr₃ 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 (AMX₃). 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}PbBr₃ (MA = CH₃NH₃⁺) 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.
3. D. R. Ceratti, A. V. Cohen, R. Tenne, Y. Rakita, L. Snarski, N. P. Jasti, L. Cremonesi, R. Cohen, M. Weitman, I. Rosenhek-Goldian, I. Kaplan-Ashiri, T. Bendikov, V. Kalchenko, M. Elbaum, M. A. C. Potenza, L. Kronik, G. Hodes, D. Cahen, *Mater. Horiz.*, **2021**, *8*, 1570-1586.

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 ¹³C-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

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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/Al₂O₃ catalysts are investigated as a function of surface modification via ALD Al₂O₃ 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 Al₂O₃ coating on the properties and performance of the 0.1% Pt/Al₂O₃ 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 National 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(NH₂) 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 CO₂ 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 CO₂ 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 IrO₂(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, IrO₂(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, CO₂ and H₂O 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 CH₄ on IrO₂(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 IrO₂(110) is highly active for the catalytic combustion of CH₄ at moderate temperatures (500-650 K), with comparable activities to PdO catalysts. Our results further show that catalytic CH₄ oxidation is mildly activated on IrO₂(110) and that the catalytic rates depend slightly inversely on the O₂ partial pressure, suggesting that the dissociative chemisorption of O₂ is more efficient than CH₄ activation and acts to block CH₄ adsorption sites. AP-XPS measurements reveal that high coverages of OH groups and CH₃O₂ species form on IrO₂(110) during CH₄ oxidation and that O-rich IrO₂(110) surfaces are maintained even under highly CH₄-rich conditions (up to 95% CH₄), consistent with efficient O₂ adsorption and site competition with CH₄. 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 IrO₂(110). Of particular significance is that earlier models did not consider surface CH₃O₂ species. Our AP-XPS results thus inspired efforts to identify additional reactions and determine the roles that various adsorbed species play during catalytic CH₄ oxidation on IrO₂(110). Our findings highlight how *operando* surface spectroscopy can provide key guidance for understanding catalytic reaction mechanisms and developing accurate kinetic models.

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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-Co₃O₄ 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., Co₃O₄, NiO, TiO₂, CeO₂, and Fe₂O₃) 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, CO₂ 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 Co₃O₄, utilizing operando surface analysis. The Pt-Co₃O₄ interfaces were prepared as powder catalysts using colloidal Pt NPs embedded on the mesoporous Co₃O₄. The two-dimensional model system is also constructed on Co₃O₄-coated Si wafer via a Langmuir-Blodgett trough to bridge the material gap. The surface of prepared Pt-Co₃O₄ is comprehensively characterized under dynamic conditions: a reducing environment (H₂ or CO) and a catalytic reaction environment (CO + O₂). 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.

Nanoscale Science and Technology Division Room 304 - Session NS+AP+BI+SS-WeM

Frontiers in Scanning Probe Microscopy Including Machine Learning

Moderators: *Wonhee Ko*, University of Tennessee, Knoxville, *Adina Luican-Mayer*, University of Ottawa, Canada

8:40am **NS+AP+BI+SS-WeM-3 Decay Rate Spectroscopy for a Direct Probe of Josephson and Andreev Currents on the Atomic Scale, Wonhee Ko**, University of Tennessee, Knoxville; *J. Lado*, Aalto University, Finland; *E. Dumitrescu*, *P. Maksymovych*, Oak Ridge National Laboratory

The tunneling current in superconducting tunnel junctions involves several mechanisms in addition to the normal-electron tunneling, such as Josephson tunneling and Andreev reflection. Identification of the tunneling mechanisms as a function of external parameters, such as barrier height, bias voltage, temperature, and so on, is the key to elucidating the characteristics of the superconductors, such as paring symmetry and topology. Here, we present a method to identify distinct tunneling modes based on the decay rate of tunneling current measured by scanning tunneling microscopy (STM) [1,2]. Precise control of the tip-sample distance in picometer resolution allows us to quantify the decay rate as a function of bias V and tip height z , with which we identified the crossover of tunneling modes between single-charge quasiparticle tunneling, (multiple) Andreev reflection, and Josephson tunneling. The method was both applied to S-I-S [1] and S-I-N [2] junctions, to unambiguously identify Josephson and Andreev currents. Moreover, mapping decay rates in the atomic resolution with STM revealed the intrinsic modulation of Andreev reflection and Josephson current. The result shows that the decay rate spectroscopy will be crucial for addressing the superconducting characteristics of the materials and their applicability for Josephson-junction devices.

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

[1] W. Ko, E. Dumitrescu, and P. Maksymovych, *Phys. Rev. Res.* **3** 033248 (2021)

[2] W. Ko, J. L. Lado, and P. Maksymovych, *Nano Lett.* **22** 4042 (2022)

9:00am **NS+AP+BI+SS-WeM-4 Machine Learning-Driven Automated Scanning Probe Microscopy: Application to Ferroelectric Materials, Yongtao Liu, K. Kelley, R. Vasudevan**, Oak Ridge National Laboratory, USA; *H. Funakubo*, Tokyo Institute of Technology, Japan; *S. Kalinin*, University of Tennessee Knoxville; *M. Ziatdinov*, Oak Ridge National Laboratory, USA

Scanning probe microscopy (SPM) has become a mainstay of many scientific fields including materials science, condensed matter physics, and so on. Machine learning (ML) and artificial intelligence (AI) have been applied to determine the physical mechanisms involved in phenomena encoded within microscopy data, enabling ML/AI to rapidly become an indispensable part of physics research. However, the real-time connection between ML and microscopy—which enables automated and autonomous experiments for microscopy imaging and spectroscopy measurements—still lags. Until now, the search for interesting functionalities in microscopy experiments has been guided by auxiliary information from microscopy to identify potential objects of interest based on human intuition; the exploration and verification of physical mechanisms depend on human-based decision making, i.e., operators determine the parameters for subsequent experiments according to the previous experiment. Here, we developed ML-driven automated experiment (AE) scanning probe microscopy (SPM) workflow to learn the functionality and mechanism in materials in an automatic manner. We demonstrate the application of deep kernel learning and hypothesis learning based workflows by investigating ferroelectric materials, including studies of domain wall dynamics, domain switching mechanism, the conductivity of topological defects, and relationship between domain structure and local properties. Using these approaches, we observe larger hysteresis opening near 180° domain walls due to the larger polarization mobility in the vicinity of the 180° walls in a PbTiO₃ sample and find that the domain switching in a BaTiO₃ thin film is determined by the kinetics of the domain wall motion, etc. We implemented these approaches in SPM for ferroelectric materials investigation, however, the workflows are universal and can apply to a broad range of imaging and spectroscopy methods, e.g., electron microscopy, optical microscopy, and chemical imaging.

Acknowledgements: This work (implementation, measurement, and data analysis) was primarily supported by the center for 3D Ferroelectric Microelectronics (3DFEM), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award Number DE-SC0021118. This work (ML development) was supported by the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility.

9:20am **NS+AP+BI+SS-WeM-5 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Direct Imaging of Light-Matter Interaction of 0-dimensional Excitonic Emitters using Tip-enhanced Scanning Probe Technique, Kiyoung Jo¹, E. Marino, J. Lynch, Z. Jiang, N. Gogotsi**, University of Pennsylvania; *P. Schuck*, Columbia University; *N. Borys*, Montana State University; *C. Murray, D. Jariwala*, University of Pennsylvania

Strong light-matter interactions of 0-dimensional emitters on plasmonic Au substrate were explored using both contact and tapping mode tip-enhanced scanning probe micro-spectroscopy. The plasmonic tip engaged with contact mode couples with the excitonic dipole in CdSe-CdS nanoplatelets, leading to strong exciton-plasmon coupling. Unlike the contact mode, the directional propagation of surface plasmon polariton from the excitonic emission of the nanoplatelets on Au as wave-like fringe patterns was probed by taking advantage of the tapping mode. Since tapping mode operates a few nanometers away from the surface, the near-field photoluminescence with in-plane wavevectors can be collected, leading to form fringe patterns propagating from the quantum plate. Extensive optical simulations proved that the fringes are the result of standing wave formed between the tip and the nanoplatelets. The effect of excitonic dipole orientation and dielectric layers on the fringe patterns were investigated by the simulation which matched with experimental results. The fringe patterns were also observed in WSe₂ nano-bubbles, and the CdSe/CdS nanoplatelet in SiO₂/Si substrate which means the phenomenon is universal in 0-dimensional emitters and various substrates. We envision that the discovery excels in understanding in-plane near-field

¹ AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient

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light signal transduction from 0-dimensional emitters toward nano and quantum photonics.

9:40am **NS+AP+BI+SS-WeM-6 Nanoscale Subsurface Depth Sensitivity of Contact Resonance Atomic Force Microscopy on Layered Films**, *Gheorghe Stan*, National Institute for Science and Technology (NIST); *C. Ciobanu*, Colorado School of Mines; *S. King*, Intel Corporation

Probing the mechanical properties is one of the basic inquiries that can reveal the structure and integrity of an isolated material or multicomponent system. At the nanoscale, due to size constraints and defects, mechanical tests become even more relevant as the properties of a part may differ by those of the whole. Over years, contact resonance AFM (CR-AFM) has proved to be a reliable AFM-based technique for nanoscale mechanical property measurements. Mostly operated into the elastic modulus range from few GPa to hundreds of GPa, CR-AFM was used to test different materials and structures at the nanoscale and considered for discerning the mechanical response of subsurface inhomogeneities and buried domains. It remains, however, to directly prove the extent of its quantitative capabilities both in terms of elastic modulus and depth sensitivity. In this work, we develop a quantitative methodology to test the elastic modulus and depth sensitivity of CR-AFM against a set of low-k dielectric bilayer films with the top layer of various thicknesses. We have analyzed the measured contact stiffness as a function of load and film thickness with both a semi-analytical model and three-dimensional finite element analysis. Both analyses confirmed the expected elastic moduli of the layered structures and provided a robust quantitative estimation of the subsurface depth and material sensitivities of CR-AFM. We also developed a correlative measurement-model analysis to assess the convoluted contributions of the structural morphology and mechanical properties to the contact stiffness used by AFM-based subsurface imaging. The results explain the inherent difficulties associated with solving concurrently the material contrast and location of subsurface heterogeneities in nanomechanical subsurface imaging.

11:00am **NS+AP+BI+SS-WeM-10 The Impact of Temperature on Viscoelastic Properties of Nanoscale Domains Within Polymer Composites**, *Bede Pittenger*, *S. Osechinskiy*, *J. Thornton*, *S. Loire*, *T. Mueller*, Bruker Nano Surfaces

The behavior of polymer composites is controlled by the properties of the components as well as the microstructure of the material. Because confinement effects and interphase formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally temperature (and time) dependent, so a full understanding requires measurements over a range of temperatures and frequencies. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

Recently, Atomic Force Microscopy based nano-Dynamic Mechanical Analysis (AFM-nDMA) was introduced. Like bulk DMA, this mode provides spectra of storage and loss modulus across frequency and temperature, allowing construction of master curves through Time Temperature Superposition (TTS). In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

11:20am **NS+AP+BI+SS-WeM-11 AFM Force Spectroscopy Combined with Machine-Learning Methods for Identifying Malaria Derived- EV Subpopulations**, *Irit Rosenhek-Goldian*, *P. Abou Karam*, Weizmann Institute of Science, Israel; *T. Ziv*, Technion - Israel Institute of Technology, Israel; *H. Ben Ami Pilo*, *I. Azuri*, *A. Rivkin*, *E. Kiper*, *R. Rotkopf*, *S. Cohen*, Weizmann Institute of Science, Israel; *A. Torrecilhas*, Federal University of São Paulo, Brazil; *O. Avinoam*, Weizmann Institute of Science, Israel; *A. Rojas*, University of Costa Rica; *M. Morandi*, *N. Regev-Rudzki*, Weizmann Institute of Science, Israel

The Malaria (*Plasmodium falciparum*) parasite releases extracellular vesicles (EVs) which modulate the mechanical properties of the host red blood cell and thus facilitate parasite action. It is understood that EVs are composed of sub-populations with different functions, but little is known of their nature and specialized function. Here, we report the use of Atomic Force Microscopy (AFM) imaging and puncture analysis, combined with state-of-the-art size separation techniques and several biochemical, microscopic and spectroscopic characterization techniques in an attempt to differentiate and characterize the different populations. Specifically, we

subjected malaria-derived EVs to size-separation analysis, using Asymmetric Flow Field-Flow Fractionation (AF4). The fractions obtained were characterized by Cryo-transmission electron microscopy (cryo-TEM), and AFM which revealed the presence of two distinct EV subpopulations - small (10-70 nm) and large (30-500 nm). Proteomic analysis revealed that the small EVs were enriched in complement-system proteins and the large EVs with proteasome subunits. In addition, Förster resonance energy transfer (FRET)-based fusion assay showed that small EVs fused to early-endosome liposomes at significantly greater levels than large EVs. Finally, AFM puncture analysis characterized by unsupervised machine-learning verified the presence of two distinct fractions with respect to mechanical behavior which correlate with the EV size groupings. These results shed light on the sophisticated mechanism by which malaria parasites utilize EV subpopulations as a communication tool to target different cellular destinations or host systems.

Surface Science Division Room 319 - Session SS1+HC-WeM

Alloy Surface Reactivity

Moderator: **Zdenek Dohnalek**, Pacific Northwest National Laboratory

8:00am **SS1+HC-WeM-1 Development of a Predictive Model for Nb₃Sn Thin Film Growth: Elucidating the Substrate-Mediated Diffusion Pathways Guiding Alloy Formation in Accelerator Infrastructure**, *Sarah Willson*, University of Chicago; *R. Farber*, University of Kansas; *S. Sibener*, University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but the required operating temperatures (< 4 K) impose a significant monetary burden. To achieve improved accelerating gradients at increased operating temperatures, efforts are underway to vapor deposit Sn on preexisting Nb SRF cavities to form Nb₃Sn thin films. However, these Nb₃Sn coatings contain high surface defect densities and stoichiometric inhomogeneities; the accelerating performance of Nb₃Sn coated cavities is directly associated with the Nb₃Sn surface morphology. Current Nb₃Sn SRF cavities, therefore, are impractical for implementation in particle accelerator facilities. The implementation of Nb₃Sn SRF cavities necessitates a comprehensive and mechanistic understanding of how to form smooth and homogenous Nb₃Sn films.

To develop a predictive growth model for Nb₃Sn grown *via* Sn vapor deposition, we aim to understand the interplay between the underlying Nb oxide morphology, Sn coverage, and Nb substrate heating conditions on Sn wettability, intermediate surface phases, and Nb₃Sn grain growth dynamics. In this work, Nb-Sn intermetallic species are grown on a single crystal Nb(100) in an ultra-high vacuum chamber equipped with *in situ* surface characterization techniques including Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy (STM/STS).

Sn adsorbate behavior on oxidized Nb was examined by depositing Sn with sub-monolayer precision at varying Nb sample temperatures (T_s). STM data of Sn deposited on a highly ordered NbO surface reconstruction reveal that the Nb T_s during deposition strongly dictates the competition between Sn incorporation and desorption during subsequent annealing. By tailoring Sn deposition parameters to suppress Sn desorption, AES and XPS data of annealed intermetallic adlayers provide supporting evidence of how Nb substrate oxidation and sample temperature impact Nb-Sn coordination. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor and substrate conditions on the growth mechanisms and alloying dynamics that ultimately enable optimal Nb₃Sn growth.

8:20am **SS1+HC-WeM-2 Surface Chemical Reactions in the Oxidation of NiCr and NiCrW Alloys**, *Petra Reinke*, *C. Volders*, University of Virginia, USA; *V. Avincola Angelici*, University of Virginia; *I. Waluyo*, *A. Hunt*, Brookhaven National Laboratory; *L. Arnadottir*, University of Oregon

The oxidation of alloys including several reactive elements is controlled by complex reaction pathways where surface chemistry, reactant transport, alloy microstructure, oxide-alloy epitaxy and other factors compete. Our work focuses on the oxidation of Ni-based superalloys frequently used in technologies subjected to a wide range of environmental stressors from chemically aggressive solutions in sea water, batteries and fuel cells to radiation in nuclear waste containers. We address the so-called "third element effect" TEE where a relatively small addition of a specific element has an outsized impact on corrosion and oxidation processes. We specifically address the initial steps in the formation of the protective oxide

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layer starting with a pristine alloy surface. Significant gaps exist in the mechanistic understanding of the initial reaction steps of their oxidation. Near ambient pressure X-ray photoelectron spectroscopy, XPS and STM were used to study the oxidation with O_2 *in operando* for a sequence of alloy compositions from Ni-5wt%Cr, Ni-15wt%Cr, Ni-30wt%Cr to Ni-15wt%Cr-6wt%W. The experiments were performed at 500 °C, $p(O_2)=10^{-6}$ mbar and reflect the initial 25 ms of oxidation at ambient conditions. The formation of Ni and Cr oxides competes under these conditions due to kinetic limitations imposed on the reaction of Cr, which is thermodynamically preferred.

The comparison of oxide evolution for four different alloys with variable Cr and W content quantifies the outsized impact of W as a minor alloying element. For the binary alloys an initial rapid increase in chromia driven by Cr-surface enrichment is followed by NiO nucleation and growth, ultimately seeding a dual-layer structure. The addition of small amounts of W in Ni-15wt%Cr-6wt%W shifts the reaction pathways towards Cr oxidation revealing a high quality chromia layer which is desirable for its protective function. Density functional theory calculations inform that W atoms adjacent to Cr sites embedded in the Ni surface create even more favorable oxygen adsorption sites. In short, a larger Cr content in the surface enhances reaction with oxygen, but the addition of W “supercharges” the reactivity of Cr by funneling the oxygen atoms into Cr sites. The surface chemistry is identified as a decisive contribution to the TEE, and is accompanied by an enhanced grain boundary driven Cr transport in the alloy to sustain chromia growth.

8:40am **SS1+HC-WeM-3 High Throughput Methods for Comprehensive Study of Alloy Segregation and Structure Sensitivity**, **Andrew Gellman, C. Fernandez-Caban, Z. Guo, R. Burnley**, Carnegie Mellon University, USA
INVITED

Comprehensive study of phenomena such as segregation in alloys or structure sensitivity in catalytic surface chemistry is hampered by the fact that the independent variables associated with these phenomena are continuous and multidimensional. In the case of alloy segregation, the relevant independent variable is alloy composition which is continuous and multidimensional in the case of ternary or higher order alloys. In the case of structure sensitivity, the possible orientations of single crystal surfaces span a continuous 2D space. Comprehensive study of these phenomena requires high throughput methods that allow rapid, concurrent measurements of surface composition and chemistry across parameter space.

Composition spread alloy films (CSAFs) have been used as sample libraries for accessing broad and continuous alloy composition spaces. CSAFs are thin alloy films deposited on appropriate substrates such that they have lateral composition gradients. A binary CSAF of components A and B can run from pure A at one end to pure B at the other. A ternary CSAF can be prepared with a triangular region that mimics a ternary composition diagram and literally contains all possible ternary alloy compositions. These alloy sample libraries are ideal for the study of surface segregation. We have used low energy He⁺ ion scattering to map segregation at 100s of alloys spanning the composition spaces of CuPdAu, CuAgAu and NiPdAu ternaries. This work has explored both equilibrium segregation over a range of temperatures and the measurement of surface segregation kinetics.

Surface Structure Spread Single Crystals (S⁴Cs) have been used as sample libraries for accessing broad and continuous ranges of single crystal surface orientations. S⁴Cs are metal single crystal disks fabricated such that one side is a section of a sphere. These usually (but not necessarily) have a low Miller index plane exposed at their center and the rest of the surface exposing all possible surface orientations lying within some polar angle (14° in our case) of the low Miller index point. By first adsorbed reactive species on the curved surface and then spatially mapping their coverage versus time, $\vartheta_{hkl}(t)$, at a given temperature we are able to extract reaction rate constants as functions of surface orientations. In this manner, we have studied the enantiospecific decomposition kinetics of D- and L-tartaric acid on all chiral Cu(*hkl*)R&S surfaces vicinal to the three low Miller index planes.

9:20am **SS1+HC-WeM-5 Unveiling the Ability of Rh Single Atoms to Enhance the Dissociation of Molecular Oxygen and Spillover to Cu**, **Volkan Cinar¹**, Tufts University; **D. Guo**, Washington State University, US; **Y. Wang, C. Easton, H. Chen**, Tufts University; **N. Ulumuddin**, Washington State University, US; **R. Hannagan**, Tufts University; **I. Waluyo**, Brookhaven National Laboratory; **J. McEwen**, Washington State University, US; **C. Sykes**, Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes such as methanol synthesis, CO oxidation, epoxidation of alkenes, and the water-gas shift reaction. As many of these reactions can take place in oxidizing environments, CuO_x surfaces have been extensively studied to better understand structure-function relationships. Single-atom alloys (SAAs) are a new type of catalyst in which small amounts of reactive dopants (Pd, Pt, Ni, Rh, etc.) are present as isolated atoms in less reactive metals such as Cu. However, literature of the behavior of these materials under oxidizing conditions is limited.

Using surface science experiments we discover that 0.005 monolayers Rh in the surface of Cu(111) enhances the rate of O₂ dissociation by ~20 times. TPD experiments are conducted using the partial oxidation of methanol to formaldehyde to titrate away the adsorbed oxygen and hence quantify the increased dissociative sticking probability of O₂ on the RhCu SAA vs. Cu(111). CO “poisoning” and annealing experiments were conducted to further investigate the role of the Rh atoms in dissociating molecular oxygen. These TPD experiments reveal that adsorption of ~1% of a monolayer of CO, which block the Rh sites and reduce the O₂ dissociation back to pure Cu(111) providing evidence that Rh is the site for O₂ activation. Furthermore, annealing the surface to 250°C, which induces the subsurface diffusion of Rh, gives the same result. Further quantification of oxygen uptake on the RhCu SAA reveals a spillover effect whereby molecular oxygen dissociates on the Rh atom sites and diffuses to sites on Cu(111). STM experiments are performed to elucidate the atomic-scale detail of this effect. The STM images reveal that on Cu(111) and the RhCu SAA, oxidation occurs at the Cu step edges, consistent with literature reports. However, for the case of the RhCu SAA, we observe features on the terraces, consistent with atomic oxygen spill over from Rh atoms. Our DFT calculations quantify the energetics of the process showing that the molecular oxygen binds to the Rh sites stronger than Cu(111) and that the activation barrier is lower as compared to bare Cu(111). Furthermore, our DFT results support the spillover of oxygen atoms from Rh site to the Cu host. Together, these results begin to shed light on the role of single metal atom dopants in promoting Cu oxidation.

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 TiO₂(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-TiO₂ 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 TiO₂ leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late

¹ SSD Morton S. Traum Award Finalist

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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 O₂ 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* O₂ 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 O₂, 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 O₂ 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} ≈ 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 Ag₁₁ 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 Ag₁₁O₁₂ nanocluster is indeed more similar to a bulk oxide

rather than to an oxidized surface, as it reaches a final hybrid structure formed of d¹⁰ Ag(I) and d⁸ Ag(III) ions which strongly resembles that of AgO bulk oxide. Furthermore, we found that the Ag 3d core level in the Ag₁₁ 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.

Thin Films Division

Room 316 - Session TF2+AP+SE+SS-WeM

ALD and CVD: Surface Reactions, Mechanisms and Kinetics

Moderator: Jessica Kachian, Intel Corporation

8:00am TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules, Amnon Rothman, D. Tsousis, S. Bent, Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-quality films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)₂) and bis(cyclopentadienyl)ruthenium(II) (RuCp₂), with O₂ as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)₂ and RuCp₂, respectively. Interestingly, pulsing TMA or DEZ, with or without exposure to H₂O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an

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increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications, Laura Nyns, A. Delabie, W. Devulder, IMEC, Belgium; J. Girard, Air Liquide, France; B. McKeown, V. Pallem, Air Liquide; T. Peissker, J. Sinha, IMEC, Belgium; N. Stafford, Air Liquide; J. Swerts, IMEC, Belgium

INVITED

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400°C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and Ge₂Sb₂Te₅ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO₂, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, *J. Am. Chem. Soc.*, 2009, **131**, 3478-3480

[2] Haider et al, *Mater. Adv.*, 2021,**2**, 1635-1643

9:00am TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO₂ investigated by gas-phase Infrared and Optical Emission Spectroscopy, M. Mione, V. Vandalon, Eindhoven University of Technology, Netherlands; A. Mameli, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands; F. Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, Netherlands; Erwin Kessels, Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO₂ using bisdiethylaminosilane (BDEAS, SiH₂[N(C₂H₅)₂]₂) and an atmospheric O₂ plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 °C, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO₂ films exhibiting material properties on par with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on -OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, HN(C₂H₅)₂). The remaining amine ligand is removed through combustion reactions activated by the O₂ plasma species leading to the release of H₂O, CO₂, CO in addition to products such as N₂O, NO₂, and CH-containing

species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO₂ during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO₂ will be discussed.

[1] M. Mione, V. Vandalon, A. Mameli, W.M.M. Kessels, and F. Roozeboom, *J. Phys. Chem. C* **125**, 24945 (2021)

[2] G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, W.M.M. Kessels, *J. Electrochem. Soc.* **159**, H277 (2012)

9:20am TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of Hf_{1-x}Al_xB₂ Coatings Below 300 °C, Kinsey Canova¹, S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson, University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB₂ films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, Hf(BH₄)₄. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary Hf_{1-x}Al_xB₂ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB₂ precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB₂ and AlB₂ grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al₂O₃ surface layer that protects the underlying film, and negligible grain growth is observed. To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB₂ precursor – which contains four boron atoms for every Hf atom – and forms AlB₂. This overcomes the probable rate limiting step of HfB₂ deposition, i.e., the associative desorption of excess boron from the growth surface as B₂H₆, and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites, Benjamin Greenberg, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson, U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 μm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al₂O₃ or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al₂O₃ nanocomposite to a compact of core/shell Al₂O₃/ZnO NPs produced by particle ALD (pALD) in a rotary reactor. Preliminary data suggest that uniform infilling of a

¹ TFD James Harper Award Finalist

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macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

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 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 H₂. 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 Cu₂O single-crystal which better mimics the Cu₂O particles present in high surface area catalysts. Scanning tunneling microscopy images of the Cu₂O(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 TiO₂ Model Supports: Anatase TiO₂ (101) and Rutile TiO₂ (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 TiO₂ model supports: anatase TiO₂(101) and rutile TiO₂(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 TiO₂ 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 Me₁ [Au₁, Pt₁, and Rh₁] on TiO₂ (110)*. arXiv preprint arXiv:2204.06991, 2022.

4:40pm HC+AS+SS-WeA-8 Boron Effect Improves Catalytic Performance on Supported Pt/SiO₂ 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 CO₂ and CH₄ 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/SiO₂ catalysts were prepared for DRM catalysis and compared with Pt/SiO₂ 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% CO₂ 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/SiO₂ 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: Pseudo-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

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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.

[2] Reece, C. and Madix, R.J., 2021. Moving from Fundamental Knowledge of Kinetics and Mechanisms on Surfaces to Prediction of Catalyst Performance in Reactors. *ACS Catalysis*, 11(5), pp.3048-3066.

[3] Libuda, J., Meusel, I., Hoffmann, J., Hartmann, J., Piccolo, L., Henry, C.R. and Freund, H.J., 2001. The CO oxidation kinetics on supported Pd model catalysts: A molecular beam/in situ time-resolved infrared reflection absorption spectroscopy study. *The Journal of Chemical Physics*, 114(10), pp.4669-4684.

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 $Ce_{1-x}Ti_xO_{2-5}$ 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 $Ce_{1-x}Ti_xO_{2-5}(111)$ 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 $Ce_{1-x}Ti_xO_{2-5}$ (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 $Ce_{1-x}Ti_xO_{2-5}$ 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 $Ce_{1-x}Ti_xO_{2-5}$ with higher Ti/Ce ratios ($Ce_{0.6}Ti_{0.4}O_{2-5}$ and $Ce_{0.5}Ti_{0.5}O_{2-5}$). 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.

[1] Z.Y. Liu, D.C. Grinter, P.G. Lustemberg, T.-D. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E.J. Crumlin, D.J. Stacchiola, J. Zhou, J. Carrasco, H.F. Busnengo, M.V. Ganduglia-Pirovano, S.D. Senanayake, J.A. Rodriguez, *Angew. Chem. Int. Ed.* **55**, (26), 7455-7459 (2016).

[2] Y. Zhou, J. Zhou, *J. Phys. Chem. Lett.* **1**, (11), 1714-1720 (2010).

[3] Y. Zhou, J. M. Perket, A. B. Crooks, J. Zhou, *J. Phys. Chem. Lett.* **1**, (9), 1447-1453 (2010).

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.

[1] J.W. Evans, P.A. Thiel, M.C. Bartelt, *Surf. Sci. Rep.* **64** 1-128 (2006).

[2] T. Duguet, Y. Han, D. Jing, B. Unal, J.W. Evans, P.A. Thiel, *PNAS* **108** 989 (2011).

[3] A. Lii-Rosales, Y. Han, D. Jing, ...K.C. Lai, J.W. Evans, P.A. Thiel, *Nanoscale* **13** 1485 (2021).

[4] K.C. Lai, Y. Han, ... P.A. Thiel, D.-J. Liu, J.W. Evans, *Chemical Reviews* **119** 6670 (2019).

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,

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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 substantially 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 Puzetzy, 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 edge 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 precision.

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 MoS₂ and WSe₂, 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. Kanqül, 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 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

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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 tuning 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-tetrakis(pentafluorophenyl)porphodilactone (trans- and cis-H₂F₂₀TPPDL) 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 framework¹, 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.

[1] Alan Y. Liu and Todd A. Sulchek, Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions with Thermally Modulated Force Spectroscopy, *Phys. Rev. Res.* 3, (2021).

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 Sumaiya¹, 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 (MoS₂), 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 MoS₂, 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), WSe₂ (semiconductor), PtSe₂ (semimetal), and α-Mo₂C (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.

¹ AVS Graduate Research Awardee

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 Al₂O₃ Decorated Platinum Surfaces, Sumandeep Kaur, H. Nguyen, L. Arnadottir, 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 Al₂O₃ 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.

¹ Lu et al. ACS Catal. 2020, 10,23, 13957

9:00am HC+AS+SS-ThM-4 Atomic-Level Studies of C₂H₄ on clean and Rh₁-Decorated Fe₃O₄(001), Panukorn Sombut, L. Puntsher, C. Wang, M. Ulrich, 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 Fe₃O₄(001)-supported Rh₁ adatoms interact with ethylene (C₂H₄) using density functional theory, combined with temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. C₂H₄ is the simplest alkene molecule, and thus a model reactant for hydrogenation and hydroformylation reactions. Our study begins with the clean Fe₃O₄(001) surface¹, where C₂H₄ 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 C₂H₄ adsorption at 2- and 5-fold coordinated Rh sites at the Fe₃O₄(001) surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two C₂H₄ molecules, while 5-fold Rh can only host a single C₂H₄ molecule. Finally, we investigate coadsorption of C₂H₄ with CO, a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

1. Bliem, R. et al. Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science* **346**, 1215–1218 (2014).

9:20am HC+AS+SS-ThM-5 How the Support Dictates the Reactivity of Fe_{O_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 (Fe₃O₄), 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 Fe₃O₄(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 Fe₃O₄(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 IrO₂(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 IrO₂(110) surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on IrO₂(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 RuO₂(110) by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped IrO₂(110). We find that the Cl-doped IrO₂(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.

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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 $p(4 \times 4)$ and $c(4 \times 8)$ 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. Rumpitz*, *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 -CH₃.¹⁻³ 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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Quantum Information Science Focus Topic
Room 302 - Session QS+AP+EM+MN+NS+SS-ThM

Systems and Devices for Quantum Computing

Moderators: Vivekananda Adiga, IBM, T.J. Watson Research Center, **Kathy-Anne Soderberg**, Air Force Research Laboratory

8:00am **QS+AP+EM+MN+NS+SS-ThM-1 Effects of Environmental Radioactivity on Superconducting Qubits**, *L. Cardani*, *Ambra Mariani*, Istituto Nazionale di Fisica Nucleare, Italy

INVITED

Environmental radioactivity was recently discovered as a potential limit for superconducting quantum bits.

We review recent works proving that ionizing radiation lowers the coherence of single qubits and induces correlated errors in qubits arrays. We also present preliminary studies showing that operating qubits in a low-radioactivity environment improves their performance. These results fuelled the interest of several European and US groups in further investigating and mitigating radioactivity for next-generation quantum processors.

Using radioactivity measurements and simulations, we estimated the separate contribution of “far” radioactive sources (cosmic rays and laboratory radioactivity) and close materials contamination (chip holder, magnetic shield, ...) on a typical chip, focussing on a qubit prototype developed within the SQMS center. We present such contributions and discuss the possibility of mitigating them in “standard” qubit laboratories or, eventually, in deep underground facilities.

8:40am **QS+AP+EM+MN+NS+SS-ThM-3 Dynamics of a Dispersively Coupled Transmon in the Presence of Noise from the Control Line**, *Antti Vaaranta*, Bluefors Oy, Finland; *M. Cattaneo*, University of Helsinki, Italy; *R. Lake*, Bluefors Oy

In this talk we present theoretical results from a complete description of transmon qubit dynamics in the presence of noise introduced by an impedance-matched resistor (50 Ohm) that is embedded in the qubit control line, acting as a noise source [1]. We derive a model to calculate the qubit decoherence rate due to the noise emanating from this noise source [2]. The resistor is treated, using the Caldeira-Leggett model, as an infinite collection of harmonic LC-oscillators making it a bosonic bath [3]. To obtain the qubit time evolution affected by this remote bath, we start with the microscopic derivation of the Lindblad master equation using the dispersive Jaynes-Cummings Hamiltonian with added inductive coupling to the bath. To solve the resulting master equation, we transform it into a block diagonal form by exploiting its underlying symmetries following Ref. 4. The block diagonalization method reveals that the long time decoherence rate is given by the slowest decaying eigenmode of the Liouvillian superoperator. Moreover, when the readout resonator is in the equilibrium thermal state, the rate of exponential decoherence of the qubit is almost exactly exponential for all times with the predicted rate given by the slowest decaying eigenmode. We also study how the decoherence rate depends on the temperature of the noise source and explore the strong and weak dispersive coupling regimes. The model captures the often used dispersive strong limit approximation of the qubit decoherence rate being linearly proportional to the number of thermal photons in the readout resonator. However, in the dispersive weak limit we predict remarkably better decoherence rates. The model parameters are completely determined by the values of the circuit components, allowing for the exact study of the dynamics on the level of each individual circuit element.

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9:00am **QS+AP+EM+MN+NS+SS-ThM-4 Accurate Microwave Characterization for Superconducting Quantum Technology**, *Slawomir Simbierowicz*, Bluefors Oy, Finland

Recent breakthroughs in quantum technology have highlighted a need for methods for accurate characterization of cryogenic microwave devices at millikelvin temperatures. In this two-part talk, I will highlight recent progress on microwave measurements at the quantum device reference

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plane including: (1) system noise characterization of amplifier chains, and (2) calibrated S-parameters of qubit drive line components. In the first part, I will discuss an impedance-matched variable temperature noise source which can be installed in a coaxial line of a cryostat. Using the method of hot/cold source with many input noise temperature points, the system noise temperatures of qubit readout amplifier cascades can be determined. I present measurement results in terms of added noise in Kelvins or photons from a four-wave (4WM) mixing traveling wave parametric amplifier (TWPA) [1], a Josephson parametric amplifier [2], 3WM TWPA, and high electron mobility transistor amplifiers [1]. In the second part of the talk, I will present measurements of the 1-port S-parameters of qubit drive line components using a data-based short-open-load calibration at a temperature of 30 mK [3]. The measurement enables us to model systematic errors in qubit state preparation due to non-idealities in qubit control lines such as impedance mismatch. We model the results using a master equation simulation of all XY gates performed on a single qubit. Our work directly addresses the gap between electrical engineering parameters of individual measurement components and performance of the quantum device itself.

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9:20am **QS+AP+EM+MN+NS+SS-ThM-5 Improving Qubit Performance Through Engineering of the Substrate-Josephson Junction Interface**, **Cameron Kopas**, H. Cansizoglu, R. Cochrane, B. Ercan, Rigetti Computing; D. Goronzy, C. Torres-Castaneda, Northwestern University; J. Oh, Ames Laboratory; A. Murthy, Fermi Lab; E. Lachman, Rigetti Computing; A. Romanenko, A. Grassellino, Fermi Lab; M. Kramer, L. Zhou, Ames Laboratory; M. Bedzyk, Northwestern University; J. Mutus, Rigetti Computing; M. Hersam, Northwestern University; K. Yadavalli, Rigetti Computing

INVITED

The performance of a superconducting qubit is often limited by dissipation and two-level systems (TLS) losses. The dominant sources of these losses are believed to come from interfaces and surfaces, likely as a result of fabrication processes, materials, or atmospheric exposure. We show that certain chemical surface treatments can be used to modify the silicon surface before Josephson junction deposition, reducing the number of strongly-coupled TLS, and improving T₁. While identifying specific microscopic sources for loss and TLS is still an open question, targeted characterization of test structures will show which physical changes correlate with performance improvements. We report chemical, structural, and low-temperature microwave characterization of superconducting qubits and films fabricated with different Si surface treatments.

11:00am **QS+AP+EM+MN+NS+SS-ThM-10 Design and Optimal Control of Superconducting Qubits to Achieve Quantum Speed Limits**, **Meenakshi Singh**, Colorado School of Mines, USA

INVITED

Fast two-qubit entangling gates are essential for quantum computers with finite coherence times. The finite interaction strength between qubits introduces a theoretical speed limit on the speed of these two-qubit entangling gates. This speed limit has been analytically found only for a two-qubit system under the assumption of negligible single qubit gate times. Here, we demonstrate such a speed limit experimentally using optimal control on two superconducting transmon qubits with a fixed capacitive coupling and finite single qubit gate times. Furthermore, we investigate the effect of additional couplings on the speed limit, both through introduction of an ancillary qubit as well as through utilization of higher transmon energy states. Finally, we discuss the generalization to many qubit systems where properly leveraging all available couplings can provide dramatic speedups.

11:40am **QS+AP+EM+MN+NS+SS-ThM-12 Atomic Scale Processing for Quantum Computing**, **Harm Knoop**, Oxford Instruments Plasma Technology, Netherlands

INVITED

With the increasing technological readiness of quantum technology (QT) the field has to start focussing on scalable fabrication methods for

quantum bits (qubits) and quantum circuits. This contribution will focus on the enabling role atomic scale processing (ASP) methods such as atomic layer deposition (ALD) and atomic layer etching could play in scaling of QT. The main focus will relate to superconducting qubits and processing of superconducting nanolayers.

Superconducting nanolayers (metals, metal-nitrides) are required for various roles in QT including use in resonators, single-photon detectors, and interconnects.¹ The electrical contacts needed to control the qubits will require non-planar connectivity using superconducting interconnects.² Adequate routes for fabrication of planar superconducting layers exist, but for 3D interconnects or through-silicon vias (TSVs), the excellent conformality of ALD nanolayers could be essential. Although for resonators conformality is not a challenge, ALD's thickness control and uniformity should allow high-quality resonators with low spread in properties. For these superconducting nanolayers, metal-nitride compounds have been identified as particularly promising since they exhibit limited surface oxidation (compared to pure metals such as Nb), combined with relatively high critical temperature (T_c) for superconductivity (e.g., as compared to Al). Despite the challenges that the synthesis of high-quality nitrides pose, plasma ALD has demonstrated the capability to deposit high-quality nitrides (e.g., low O content, high electrical conductivity).³ Furthermore, substrate-biased plasma-ALD offers unique opportunities to obtain and tune high-quality nitrides.⁴ For removal of surface oxides or smoothing of resonator surfaces and interfaces, approaches combining ALD and ALE could be of interest.⁵ Both ALD and ALE are envisaged to be key tools to allow scaling of these devices and advance the QT field.

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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).

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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 $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ 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. Czetti*, *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 $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ coating in protective atmosphere and air up to 1400 °C. The as-deposited coating crystallizes in an fcc- $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ solid solution with a preferred $\langle 311 \rangle$ orientation. Alternating Cr-enriched and Ta-enriched nano-layers are identified in the cross-section, which arise from the three-fold rotation during deposition. $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ powder is stable in protective atmosphere up to temperatures of ~ 1200 °C, where a transformation into fcc- $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ to t- $\text{Cr}_{1.2}\text{Ta}_{0.8}\text{N}$ sets in. Vacuum annealing of $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a

texture change to $\langle 200 \rangle$ at 1270 °C and the transformation to t- $\text{Cr}_{1.2}\text{Ta}_{0.8}\text{N}$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t- CrTaO_4 and r- Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc- $\text{Cr}_{0.74}\text{Ta}_{0.26}\text{N}$ grains close to the substrate interface, a porous transition layer of r- Cr_2O_3 and t- CrTaO_4 and a dense r- Cr_2O_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-Initio 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 ($\text{B}/\text{M} > 2$) [2] but the recent addition of understoichiometric MB_2 coatings ($\text{B}/\text{M} < 2$) 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

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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 $Ti_xZrNbTaFeBy$ 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 TiB_2 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 $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.5}B_{61.1}$ 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 Trogia, 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 National 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

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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 heterogeneous 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 $\text{Cu}_x\text{Rh}_{3-x}(\text{BTC})_2$ 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 $\sim 3690 \text{ cm}^{-1}$ 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 de-coordinated 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 pseudomorphic 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 be 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 faceted 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

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. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Thin Films Division

Room 316 - Session TF1+SE+SS-ThM

Nucleation, and Interface Phenomena in Thin Films

Moderators: *Adrie Mackus*, Eindhoven University, Netherlands, *Qing Peng*, University of Alabama

8:00am **TF1+SE+SS-ThM-1 Opportunities of Complex Oxides Prepared by Atomic Layer Depositions**, *P. Sallés, P. Machado, Mariona Coll*, ICMAB-CSIC, Spain **INVITED**

The rapid development of electronic devices, telecommunication systems, and sensors pushes new functional demands with increasingly stringent requirements like flexibility, light weight, and miniaturization. Transition metal oxides present the richest variety of functional properties due to the large diversity of chemical compositions and structures that they can offer. However, the preparation and manipulation of crystalline yet bendable functional complex oxide membranes has been a long-standing issue as they require specific crystalline substrates and high temperature treatments. We have developed a facile chemical route based on the use of $\text{Sr}_3\text{Al}_2\text{O}_6$ (SAO) sacrificial layer to detach oxide thin films of various

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compositions from the growing substrate and enable their transfer to flexible substrates.[1] Meticulous chemical and structural study of the SAO film have allowed us to identify the formation of an amorphous SAO capping layer and carbonates upon air exposure, which dictate the crystalline quality of the subsequent oxide film growth.[2] Judicious cation substitution in SAO enabled both decreasing reactivity with ambient moisture and modulating the strain state of the subsequent heterostructures grown on it. Upon detailed investigation of oxide adhesion on polymeric substrates and sacrificial etching (figure 1), crystallinity, surface morphology, interface cation diffusion, mechanical and electrical properties of transfer printed heteroepitaxial $\text{BiFeO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ membranes have been studied and compared with rigid substrates. From this work it is envisaged many new opportunities to prepare artificial oxide heterostructures and devices offering a whole new dimension for electronics and beyond.

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8:40am TF1+SE+SS-ThM-3 An Atomic-Scale Study of Si Epitaxial Growth on Cl-Si(100), Azadeh Farzaneh, University of Maryland, College Park; R. Butera, Laboratory for Physical Sciences

Atomically-precise fabrication techniques utilize a scanning tunneling microscope to lithographically define electronic devices and components, where a monatomic layer of H or Cl adsorbed on Si(100) acts as a resist. Unlike traditional resists, these monatomic resists either desorb or remain at the growth front during subsequent growth of Si capping layers. While the body of literature extensively explores Si deposition and subsequent diffusion on H-Si(100), Cl-Si(100) has remained relatively unexplored. A detailed understanding of the thin film growth mechanism enables atomic level control of the interface, which starts with diffusion of adatoms in dilute regimes on the surface. Here we explored the initial stages of Si growth on Cl-Si(100) and characterized thin Si films (~25 nm) grown on this surface. The activation energy for Si adatom diffusion on Cl-Si(100) was extracted from STM observations combined with simulations of a simple random walk model rooted in the mechanism of Si chain formation at different temperatures. Ex-situ characterization of thin Si films grown on Cl-Si confirmed the formation of crystalline layers and the near complete removal of Cl from the Si matrix. The epitaxial film obtained on Cl-Si(100) and absence of Cl from the interface confirm Cl as a viable resist for current atomically precise fabrication schemes. This opens up new pathways for introducing new chemistries and materials into the picture.

9:00am TF1+SE+SS-ThM-4 The Effect of Oxygen Plasma on the ZnO Growth on Polymer Substrates During Plasma-Enhanced Atomic Layer Deposition, Lisanne Demelius, Graz University of Technology, Austria; M. Blatnik, CEITEC – Central European Institute of Technology, Brno University of Technology, Czechia; K. Unger, Graz University of Technology, Austria; P. Parlanti, M. Gemmi, Istituto Italiano di Tecnologia, Center for Materials Interfaces, Italy; A. Coclite, Graz University of Technology, Austria

Atomic layer deposition (ALD) is a powerful technique to deposit highly conformal thin films the thickness of which can be precisely controlled. However, the use of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material.

Plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates.

Our work contributes to a deeper understanding of how oxygen plasma applied during PE-ALD affects film formation, nucleation, and interface formation of ZnO on polymer substrates. In-situ spectroscopic ellipsometry was used as the main technique to monitor the PE-ALD growth of ZnO on selected polymer thin films. To better understand how the chemical structure of the polymer influences plasma-substrate interactions and ZnO thin film formation, both crosslinked and linear polymers exhibiting varying degrees of reactivity with the ALD precursor were studied.

Our results show that while the plasma efficiently activates the polymer surface to enable rapid ZnO nucleation, it can also cause significant substrate etching that dominates the initial stage of growth until, at a certain point, ZnO growth takes over and the regime of normal ALD growth behavior is entered. The strength and extent of etching strongly depends on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

A closer examination of the first 25 PE-ALD cycles showed that, on the nanometer scale, the simultaneous etching of the polymer and ZnO nucleation leads to a certain degree of intermixing at the interfaces, the extent of which depends on the type of polymer. It was also revealed that, during the first few cycles, no stoichiometric ZnO is yet formed but instead Zinc is found to be bonded to hydroxyl groups and presumably oxygen-carbon species from the polymer, forming hybrid bonds. This points to a strong interaction between the polymer substrate and the forming ZnO, which can be expected to result in good film adhesion, a property that is critical in all applications involving mechanical stress and strain.

9:20am TF1+SE+SS-ThM-5 Measuring Local Atomic Structure Variations Through the Depth of Ultrathin ALD Aluminum Oxide, Nikhila Paranamana, M. Young, R. Gettler, H. Koenig, S. Montgomery-Smith, X. He, University of Missouri, Columbia

Understanding the atomic structure of ultrathin (<20 nm) atomic layer deposition (ALD) coatings is critical to establish structure property relationships and accelerate the application of ALD films to address technological needs. Previous studies have measured the atomic structure of nanoscale ALD films using cryogenic electron diffraction with a large (~200 nm) beam diameter. However, for ultrathin ALD coatings, these measurements provide only ensemble average structural information and cannot be used to directly measure differences in atomic structure through the depth of the ALD film. In this study, we localize the electron beam to a small (~ 5 nm) spot size using cryogenic scanning transmission electron microscope (STEM) and we collect electron diffraction data at multiple points along the depth of a 12 nm thick ALD AlO_x film deposited onto a CNT substrate without a contribution from the substrate. We couple these diffraction measurements with pair distribution function (PDF) analysis and iterative reverse Monte Carlo-molecular statics (RMC-MS) modeling to compare atomic structure metrics at different positions in the film depth. We interpret the modeling results considering the 3D concentric cylindrical sample geometry of a CNT with uniform AlO_x coating. These measurements confirm a two-phase bulk/interface structural model proposed previously for ALD AlO_x , and indicate that the interfacial layer at the CNT- AlO_x interface is 2.5 nm thick – five times larger than previously reported. This report demonstrates direct measurement of atomic structural variations across ultrathin films that is of broad interest for understanding local differences in atomic structure across material interfaces.

9:40am TF1+SE+SS-ThM-6 Interfacial Reactions and Energy Transfer in Sputter Deposited Thermite Reactive Nanolaminates, Chloe Skidmore, J. Maria, Pennsylvania State University

Cost effective energetic materials with highly tunable ignition and actuation have important applications in both military and commercial sectors. Recently, interest has grown in nanoenergetic composites due to their potential as stand-alone explosives with greater reliability, heat release, and combustion efficiency. Thermite is a versatile inorganic energetic of specific significance due to the highly exothermic reduction-oxidation reaction that occurs between metal and oxide constituents, resulting in self-sustaining heat production. However, if the high energy release and improved tunability provided by the diverse chemistries of inorganic energetics is to be utilized, a fundamental understanding of the initiation and propagation processes in new nanoenergetic materials such as thermite is necessary. Thin film deposition of multilayered stacks of alternating metallic and oxide layers with well defined interfaces offers a streamlined process to observe energy transduction and the chemical reactions that mitigate interface reactions. These multilayered stacks, termed reactive nanolaminates (RNLs), facilitate control over reactant thickness, diffusion distance, interface quality and the total material involved, while also reducing premature intermixing of metal and oxide layers. This presentation explores energy release in sputter deposited CuO-Mg RNLs as a function of bilayer thickness, plasma energetics, and metal-oxide layering sequence. These samples are analyzed via in-situ high temperature x-ray diffraction (XRD) and differential scanning calorimetry (DSC), as both probe the oxygen exchange process by structure evolution and energy production, respectively. The bulk properties associated with the Mg-CuO thermite system suggests extensive oxygen dissolution in the starting metal and the possibility of transient eutectic liquid formation during reaction. XRD results indicate that CuO/Mg RNLs exhibit eutectic liquid formation during reaction, with Cu_xMg_y intermetallics temporarily appearing around 565°C. DSC analysis reveals exotherm maxima at temperatures associated with critical points in the Mg-Cu phase diagram.

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More precisely, as interfacial area is increased the max exothermic peak shifts from $\sim 650^{\circ}\text{C}$ (T_m Mg) to $\sim 565^{\circ}\text{C}$ (T_m Mg₂Cu) before finally occurring at $\sim 483^{\circ}\text{C}$ (T_m eutectic Mg/Mg₂Cu). Preliminary DSC analysis also suggests that, relatively speaking, sputtering energetics resulting in smoother, more crystalline Mg interlayers, shifts the maximum exothermic peak to higher temperatures. These findings provide insight into the mechanisms of energy transfer in thermite RNLs, allowing for highly tunable, reliable energetic materials.

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 Ka and K β 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+1AX_n, 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 ~8 μ m 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 fragrances [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 methylacetoacetate (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 LaTiO₃/SrTiO₃ (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

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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 Nb_xO_y 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-O₃ 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-O₃) exposures of WSe_2 and use the UV-O₃ functionalized WSe_2 surfaces as substrates for ALD of HfO_2 . We report two UV-O₃ 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 oxy-selenide 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-O₃ 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-O₃ 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/SiO₂ and SiC/SiO₂ 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

¹ Gaede Langmuir Award Winner

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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 patterned 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 outsized 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.

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 Al₂O₃ ALD on LiMn₂O₄ (LMO) is much different compared to conventional surfaces such as hydroxylated SiO₂. For instance, LMO does not have surface hydroxyls under typical ALD conditions. During initial Al₂O₃ ALD cycles, trimethyl aluminum reacts with Mn-O bonds and reduces surface Mn ions generating C₂H₆. Al₂O₃ 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 Al₂O₃ ALD growth per cycle (GPC) on LMO varies by 30x among 5 Al₂O₃ ALD precursors that exhibit essentially the same GPC on SiO₂. We next examined the surface chemistry for Al₂O₃ and AlF₃ 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_yO₂, 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.

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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 $\text{TiO}_2(101)$** , 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 $\text{TiO}_2(101)$ from tetrakis(dimethylamido) hafnium (TDAMHF) and water precursors at both high (500 K) and low (300 K) surface temperature as well as high ($\sim 10^{-1}$ mbar) and low ($\sim 10^{-6}$ mbar) pressure.

Generally, we find that the initial ALD process on $\text{TiO}_2(101)$ 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 $\text{TiO}_2(101)$ 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 .

[1] Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. *J. Appl. Phys.* 2013, **113**, 021301

[2] Johnson, R. W.; Hultqvist, A.; Bent, S. F. *Materials Today* 2014, **17**, 236

[3] Zaera, F. *Coord. Chem. Rev.* 2013, **257**, 3177

[4] Richey, N. E.; De Paula, C.; Bent, S. F. *J. Chem. Phys.* 2020, **152**, 1

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 Fe_2O_3 is well-studied process. Fe_2O_3 has numerous applications, for example in catalysis or as a ferroelectric material. While many Fe_2O_3 ALD processes have been reported, almost all of those use an iron precursor in combination with strong oxidizers such as H_2O_2 , O_3 , or O_2 plasma. Recently, ALD of Fe_2O_3 on Pt substrates has been demonstrated using just O_2 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 (SiO_2 , Al_2O_3 , Au); hence, it is hypothesized that the Pt substrate creates reactive oxygen species *in situ*, effectively catalyzing the reaction to grow Fe_2O_3 . Intriguingly, the activation continues after the Pt substrate has been completely covered by Fe_2O_3 . 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 Fe_2O_3 crystal structure. X-ray photoelectron spectroscopy results show a clear correlation between the amount of deposited Fe_2O_3 and the Pt surface coverage. To study the kinetics and mechanistic steps of the process, quadrupole mass spectrometry (QMS) was employed. H_2O (m/z 18) CO (m/z 28, which is also N_2) and CO_2 (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 O_2 , the model captures adsorption, transport and desorption of the oxygen in the layer before (O_2) 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.

[1] Singh, Joseph A., et al. "Area-selective atomic layer deposition of metal oxides on noble metals through catalytic oxygen activation." *Chemistry of Materials* 30.3 (2018): 663-670.

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.

[1] K. Yamanaka, M. C. Vestergaard, E. Tamiya, *Sensors (Switzerland)* **2016**, *16*, 1761.

[2] A. Bolotsky, D. Butler, C. Dong, K. Gerace, N. R. Glavin, C. Muratore, J. A. Robinson, A. Ebrahimi, *ACS Nano* **2019**, *13*, 9781.

[3] R. Muralidharan, V. Chandrashekar, D. Butler, A. Ebrahimi, *IEEE Sens. J.* **2020**, *20*, 13204.

[4] D. Butler, D. Moore, N. R. Glavin, J. A. Robinson, A. Ebrahimi, *ACS Appl. Mater. Interfaces* **2021**, *13*, 11185.

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 1.5 μm . 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 $\text{MoS}_2/\text{MXene}/\text{CNT}$ 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 $\text{MoS}_2/\text{MXene}$ 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 matter 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. MoS₂ has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS₂ is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G_{\text{H}_2, \text{ads}}^{\text{H}}$, 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 H₂ evolution, the catalytic performance of MoS₂ 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 MoS₂. This success centered on obtaining a more thermoneutral $\Delta G_{\text{ads}}^{\text{H}}$ 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 (PtSe₂) and platinum ditelluride (PtTe₂) to construct the thinnest elements of skintronics - electronic tattoos. The PtSe₂ and PtTe₂ e-tattoos that can be grown at comparably low temperatures (400°C) 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 unsusceptible 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.

Plasma Science and Technology Division

Room 305 - Session PS1+MS+SS-FrM

Modelling of Plasmas and Plasma Driven Processes, and Plasma-Surface Interactions II

Moderators: *Tetsuya Tatsumi*, Sony Semiconductor Solutions Corporation, Japan, *Yu-Hao Tsai*, TEL Technology Center, America, LLC

8:20am **PS1+MS+SS-FrM-1 Helium and Hydrogen Plasmas Interaction with Si-Based Materials for Advanced Etch Applications: Insights from MD Simulations**, *Emilie Despiau-Pujo, V. Martirosyan, F. Pinzan*, Univ. Grenoble Alpes, CNRS, LTM, France; *F. Leverd*, ST Microelectronics, France; *O. Joubert*, Univ. Grenoble Alpes, CNRS, LTM, France

Featuring ultrathin layered materials in complex architectures, advanced nanoelectronics structures must be etched with a nanoscale precision and a high selectivity to preserve the electronic properties of active layers. Plasma-induced damage and reactive layers formed during the etch process must thus be carefully controlled, a challenge which cannot be addressed by conventional continuous-wave plasmas. To achieve uniform and damage-free etching, one possible route is to use sequential ion modification and chemical removal steps. In the first step, the material to be etched is exposed to a hydrogen (H₂) or helium (He) CCP or ICP plasma; in a second step, the modified layer is selectively removed by wet cleaning (HF bath) or exposure to gaseous reactants only (eg. NF₃/NH₃ remote plasma). In this paper, Molecular Dynamics (MD) simulations are performed to study the interaction between He and H₂ plasmas with Si, Si₃N₄ and SiO₂ materials. The objective is to better understand the light ion

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implantation step, and clarify the influence of the ion energy and ion dose on the structural and chemical modifications of the surface. Simulations of low-energy (15-200 eV) He⁺ and H_x⁺ bombardment lead to a self-limited ion implantation, followed by the formation of a modified layer of constant thickness at steady state. The modified layer thickness increases with the incident ion energy and only few sputtering is observed in the ion energy range considered here. The detailed structure of the modified materials at steady state will be discussed and compared during the presentation. Simulation predictions will also be confronted to experimental results of He⁺ and H⁺ implantation of Si₃N₄ and SiO₂ layers, followed by HF wet cleaning.

8:40am **PS1+MS+SS-FrM-2 Efficient Parametric Nonlinear Model Reduction of Low Temperature Plasma Applications, Abhishek Verma**, Applied Materials Inc.; K. Bera, S. Rauf, Applied Materials, Inc.

Low temperature plasma simulations are playing an increasingly important role in system discovery, design and decision making in industrial applications, with greater demands for model fidelity. Often, high fidelity simulation models necessitate fine spatiotemporal resolution, coupled multiphysics etc., leading to higher computational cost. This precludes the integration of such models for many important scenarios where the models are required to be simulated very rapidly and multiple times. To overcome this challenge, we present a deep learning based non-linear model order reduction method used to develop surrogate models for low temperature plasma applications. We propose a computationally practical approach for model order reduction that is non-intrusive and purely data driven in nature, using convolutional autoencoders and recurrent neural networks from deep learning. Our numerical experiments on radio frequency powered capacitively coupled plasmas shows that deep learning-based model can learn an efficient latent space representation of spatial and temporal features of plasma dynamics. The learning data is generated by the full order model that includes continuity equations for charged and neutral species, drift-diffusion approximation for electron flux, momentum conservation equation for ions coupled with Poisson's equation. The proposed method is extended to parametric model by embedding parametric information into the latent space for broader applications. Finally, we demonstrate the effectiveness of proposed approach over linear-subspace method for low temperature plasma applications.

9:00am **PS1+MS+SS-FrM-3 Novel Approaches to Generate Missing Data for Plasma Chemistry Modelling, Sebastian Mohr**, Quantemol Ltd., UK; M. Hanicinec, A. Owens, J. Tennyson, University College London, UK

Plasma simulations are a standard method in both industrial and academic settings to optimise plasma processes and gain a better understanding of the underlying physical and chemical processes. To get useful results, comprehensive and reliable data on chemical processes in the plasma are vital. These usually need to be collected from multiple sources including journal articles. To shorten this process, several centralised plasma chemistry databases were collected in recent years. The Quantemol-DB database [1] started as simply a collection of reaction data. Since then it has been enhanced by tools to quickly collect and test data for specific gas mixtures such as an automatic set generator and a global model. Here, we introduce new additions to this tool set.

While for some commonly used gases such oxygen or CF₄, vast data on heavy particle reactions are available, they are missing for more exotic or newly used gases. In such cases, reactions are usually included by analogy to known gases, including the rate coefficients for these estimated reactions. However, the rate coefficients can actually differ significantly for similar reactions between different molecules. This is especially true for neutral-neutral reactions which can have a significant influence on the chemical composition of the plasma. *Ab initio* calculations are very time-intensive if possible at all, so to get better estimates of missing rate coefficients, we developed and tested a machine learning regression model [2] which gives rate coefficients for binary heavy particle reactions based on fundamental physical and chemical properties of the reactants and products.

Apart from reactions between particles, radiative transitions of excited states also play an important role in plasmas. They determine the density of excited states and provide the flux of photons to surfaces which might induce additional surface reactions. Furthermore, optical emission spectra are an important diagnostic to obtain plasma parameters. In order to incorporate radiative transitions into our set generation tools, we have created a new database of atomic and molecular lifetimes called LiDa which is linked to QDB and enhances our global model to allow for excited state lifetimes. In due course we will also provide plasma emission fluxes.

[1] Tennyson et al., *Plasma Sources Sci. and Technol.* **26**, 055014 (2017)

[2] <https://github.com/martin-hanicinec-ucl/regreschem>

9:20am **PS1+MS+SS-FrM-4 Particle-in-Cell Modeling of Electron-Beam Generated Low Electron Temperature Plasma, Shahid Rauf**, Applied Materials, Inc.; D. Sydorenko, University of Alberta, Canada; S. Jubin, W. Villafana, S. Ethier, A. Khrabrov, I. Kaganovich, Princeton University Plasma Physics Lab

Plasmas generated using energetic electron beams are known to have low electron temperature and plasma potential, attributes that are particularly useful for atomic-precision plasma processing. [1] It has been demonstrated that electron beam plasmas cause significantly lower degradation of single layer carbon nanotubes than conventional radio-frequency plasmas. [2] In addition, they have been used to etch materials with atomic precision. [3] Electron beam produced plasmas are typically confined using a static magnetic field and operated at low gas pressures. Previous hybrid modeling of these plasmas confirmed that plasma transport can be non-classical in this parameter regime. [4] The electron transport coefficients were empirically tuned in this hybrid model using experimental measurements, and this hybrid model is only expected to be valid over a narrow range of gas pressure and magnetic field. A self-consistent 2-dimensional particle-in-cell model of electron beam produced plasmas is described in this paper. The model examines the creation and evolution of plasma in low pressure (10 – 40 mTorr) Ar gas on injection of an energetic electron beam (2 keV). Low frequency waves are initially observed as the plasma forms and expands across the magnetic field. These waves radiate outwards from the beam axis towards the chamber walls. The waves gradually disappear as the plasma fills the chamber volume. The final steady-state plasma is well-confined by the magnetic field with the plasma more constricted around the beam axis at lower pressure and higher magnetic field. The electron temperature is less than 1 eV for the range of conditions examined. Physical and energy transport in the plasma (i.e., ambipolar diffusion and thermal conduction) are observed to scale differently with magnetic field and gas pressure. The charged species density is, for example, found to be more confined near the electron beam axis than the electron temperature. The effect of gas pressure, magnetic field and beam current are examined in the paper. The impact of these parameters on electron density, plasma potential and electron temperature are found consistent with probe-based experimental measurements. [4]

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[2] Jagtiani et al., *J. Vac. Sci. Technol. A* **34**, 01B103 (2016).

[3] Dorf et al., *J. Phys. D: Appl. Phys.* **50**, 274003 (2017).

[4] Rauf et al., *Plasma Sources Sci. Technol.* **26**, 065006 (2017).

9:40am **PS1+MS+SS-FrM-5 Modeling Edge Effects in Wafer Etching with VSim, Daniel Main, J. Cary, T. Jenkins**, Tech-X Corporation

Plasma processing chambers for the etching of wafers are often used to create a uniform etch along most of the wafer. In such a chamber, a plasma is created using a RF source via Capacitive Coupling (CCP) or Inductive Coupling (ICP). The source region is often far from the wafer (thousands of electron Debye lengths) so that the plasma is nearly uniform for most of the chamber. Therefore, the physics that requires a kinetic approach occurs near the wafer (within a few hundred Debye lengths). An important part of the process is the acceleration of the ions due to the sheath that forms near the wafer. However, the discontinuity in the boundary near the edge of the wafer leads to a non-uniform sheath and hence non-uniform ion velocities impacting the wafer. One way to make the sheath more uniform is to place a "focus ring" (FR) near the wafer edge. To model the essential physics near the wafer, including the effect of the FR on the sheath dynamics, we have used the electromagnetic, fully kinetic, particle-in-cell simulation package VSim. The simulation includes electrons, argon ions and neutral argon gas. We also include collisions between electrons and neutral species, secondary emission off the wafer, and the self-consistent calculation of the electric field, including a proper inclusion of the wafer and FR dielectric constants. Since the electric field is determined by Poisson's equation, including a full kinetic treatment of the electrons is essential for computing the sheath physics, and hence ion dynamics, correctly. Because of the small spatial and time steps required for a fully kinetic model, we include about half the wafer up to the edge and about 200 Debye lengths above the wafer. We inject both electrons and ions (modeled as drifting Maxwellians) at the boundary opposite the wafer using incoming-flux boundary conditions, which ensure a smooth transition from the assumed infinite plasma reservoir outside the simulation into the

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simulation domain. We use Rejection-Sampling theory to compute the correct incoming-flux velocities of the injected particles. The boundary that includes the wafer is an absorbing boundary; electrons and ions accumulate on the dielectrics at this boundary. We show that elastic collisions tend to create a more symmetric Ion Angular-Energy Distribution (IAED) function about the normal. Finally, we demonstrate the role the focus ring has on the IAED and sheath dynamics.

10:00am **PS1+MS+SS-FrM-6 A Study on Dielectric Material Etching in Cryogenic Process Based on Atomistic Simulation**, *Junghwan Um*, Yonsei University, Korea; *S. Cho*, Samsung Electronics Co., Inc., Republic of Korea; *K. Kang*, Yonsei University, Korea

The adsorption of H₂, H₂O and HF in each membrane was calculated using molecular dynamics and DFT as parameters necessary to know the adsorbate concentration on the surface according to the temperature of SiO₂ and Si₃N₄. After obtaining the parameters for reaction rate of the pathway in which the chemical reaction of each film material appears, the reaction rate according to the surface temperature of the film material was calculated using an analytic model and previously reported experimental results. As a result, the reaction rate according to the surface temperature of SiO₂ and Si₃N₄ was obtained, and the reaction rate increased by decreasing the temperature was presented as a quantitative value. Finally, through the results of this study on the temperature dependence of the surface reaction, the understanding of the cryogenic process was helped, and the overcoming of aspect ratio dependent etching in deep contact was considered.

10:20am **PS1+MS+SS-FrM-7 Machine Learning Based Model for a RF Hollow Cathode Discharge**, *K. Bera*, *A. Verma*, *Sathya Ganta*, *S. Rauf*, Applied Materials, Inc.

Radio-frequency (RF) hollow cathode discharges (HCD) at low to moderate pressures have gained significance for advanced plasma processes in the semiconductor industry. HCDs form in cylindrical cavities in the cathode, and one can use an array of such cavities to create large area HCDs. A neutral-network based reduced order model for HCDs is discussed in this paper, where this reduced order model is trained using results from Particle-in-Cell/Monte Carlo Collision (PIC/MCC) simulations of single hollow cathode holes. In this PIC/MCC model, using charge density of particles, Poisson equation is solved for electric potential, which yields the electric field. Using this electric field, all charged particles are moved. The PIC/MCC code considers particle collisions with each other and with neutral fluid using a Monte Carlo model. RF hollow cathode behavior is simulated and characterized for different hole size, pressure, RF voltage, frequency, and secondary electron emission coefficient. The plasma penetrates inside the hollow cathode hole with increase in pressure, leading to plasma enhancement. The synergistic effect of RF sheath heating and secondary electron acceleration on hollow cathode discharge has been observed. For improved computational efficiency, a reduced order modeling framework has been developed based on neural network using plasma model parameters. Different methodologies have been explored in selecting and preprocessing physical data to train and validate the neural network. The temporal variation of voltage-current characteristics as well as that of spatial profile of plasma variables (density, temperature, etc.) have been used to train the neural network model. The predictions of trained neural network model compare reasonably well with that of the underlying physical model observations in PIC/MCC simulations. The neural network framework is being applied to determine the collective behavior of an array of RF hollow cathode holes for large area HCDs.

10:40am **PS1+MS+SS-FrM-8 Molecular Dynamics Simulations of Plasma-Enhanced Atomic Layer Etching of Silicon Nitride Using Hydrofluorocarbon and Oxygen Plasmas**, *Jomar Tercero*, Osaka University, Japan; *A. Hirata*, Sony Semiconductor Solutions Corporation, Japan; *M. Isobe*, *K. Karahashi*, Osaka University, Japan; *M. Fukasawa*, Sony Semiconductor Solutions Corporation, Japan; *S. Hamaguchi*, Osaka University, Japan

Molecular dynamics simulations were performed to study the influence of oxygen (O₂) in the hydrofluorocarbon (HFC) plasma-enhanced atomic layer etching (ALE) of silicon nitride (Si₃N₄). ALE is known to etch a surface with atomic-scale control and precision. Its in-depth understanding is essential for the advancement of fabrication technologies for semiconductor devices. It was presented earlier that such a Si₃N₄ ALE process can lead to an etch stop due to the accumulation of C atoms on the surface [1]. It was then shown that, by introducing an O₂ plasma irradiation step, a stable etch was observed and the etch stop was prevented [2]. In this study, molecular dynamics (MD) simulations were used to clarify the interaction

mechanisms of an O₂ plasma with the modified Si₃N₄ surface during the HFC-based ALE process. To do this, CH₂F radicals were used in the adsorption step. It was then followed by Ar⁺ bombardment in the desorption step. Subsequently, O₂ plasma was introduced as an additional step to help the removal of the remaining HFC species. This series of steps corresponds to one ALE cycle. Our simulations have shown that, during the desorption step of the first ALE cycle, HFC species assist the removal of the Si and N atoms of the Si₃N₄ by the formation of volatile by-products such as SiF_x, CN_x, and NH_x species. On the other hand, due to the momentum transfer from incident Ar⁺ ions, some HFC species were pushed into the bulk layer, forming chemical bonds with Si and N atoms therein. By the addition of the O₂ plasma irradiation step, it was observed that HFC species interact with O atoms adsorbed on the surface. The removal of C atoms was also enhanced by the formation of CO_x. In this way, our MD simulations have shown that the additional O₂ plasma irradiation step prevents the etch stop and allows stable Si₃N₄ ALE cycles.

References

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11:00am **PS1+MS+SS-FrM-9 Understanding Plasma Etch Mechanism of Low-k Materials Under Low Temperature Substrates with Fluorine-Based Precursors**, *Daniel Santos*, Tokyo Electron America; *C. Vallee*, SUNY Polytechnic Institute, Albany; *P. Wang*, Tokyo Electron America

Plasma etching of ultra-low-k materials at aggressive back end of line (BEOL) nodes has become increasingly challenging as plasma induced damage becomes a significant challenge to overcome. Conventional reactive ion etch (RIE) processes usually occur at a temperature near room temperature in which diffusion of radicals will damage low-k materials surface. Alternatively, to limit diffusion mechanisms and prevent damage, cryogenic cooling of a substrate sub <-100 C can be used. The purpose of this research is to understand how to leverage the range between room temperature and cryogenic temperatures when using fluorine-based plasmas.

For this work we use a 300mm dual frequency TEL CCP chamber equipped with a low-temperature electrostatic chuck to conduct our experiments. Furthermore, we use in-situ OES, ex-situ XPS, and ellipsometry to understand the plasma surface interactions and observe change in etch rates, fluorine content and composition. We find the choice of between different Fluorine molecules plays a critical role in changing the surface fluorination in dielectric materials, and opposite results have been observed. When using NF₃ the etch rate of low-k 3.0 increases from 200 nm min⁻¹ at 15C to 350 nm min⁻¹ at -40C but the etch rate of thermal oxide remains 10 nm min⁻¹ at all ranges between which displays an increase in selectivity between the films. Opposite of that, when using C₄F₈ we observe the etch rate decrease from 135 nm min⁻¹ at 15C to 90 nm min⁻¹ at -40C with decreasing temperature suggesting that we enter a higher polymerization regime. We have concluded that different temperature threshold can be obtained, for same plasma parameters, for switching from deposition to etching regime and this behavior depends on fluorine molecule and substrate material composition, which also induces a modification of the selectivity. Using this approach, we try to understand the plasma surface reactions for the fluorine molecules as a function of their triple point temperature, surface saturation with F atoms, and condensation mechanisms.

11:20am **PS1+MS+SS-FrM-10 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons**, *Chon Hei Lam*, *M. Carruth*, University of Texas at Austin; *Z. Chen*, *J. Blakeney*, *P. Ventzek*, *S. Sridhar*, Tokyo Electron America Inc.; *J. Ekerdt*, University of Texas at Austin
The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. Plasma-assisted ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove a limited amount of material. ALE may provide fine control over the etch rate through the "layer-by-layer" process and can limit physical damage to the substrate. Since silicon nitride films are a likely component in self-aligned multiple patterning schemes, we explore silicon nitride ALE by utilizing undissociated fluorocarbon (CF₄ and CHF₃) adsorption followed by argon ion bombardment. The impact of gas precursors, energetic ion energy, substrate temperature, and the nature of the surface chemical

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modification are discussed. We follow the surface chemistry and monitor structural damage during ALE with various *in situ* probes (X-ray photoelectron spectroscopy and spectral ellipsometry). Using CHF_3 to illustrate surface modification and argon ion bombardment to affect removal in concert with the spectroscopic probes we demonstrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 100 °C (Fig 1). The silicon nitride films were exposed to CHF_3 at 4 mTorr for 60 s in the fluorocarbon adsorption step followed by argon ion bombardment. The F 1s peak appears after argon ion bombardment (4 min, 200 eV) at 100 °C. After the first ALE cycle, a C-F bond was detected in C 1s spectra at high binding energy (300 eV) (Fig 2a). The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon. The ALE process also leads to nitrogen depletion which is shown in the N 1s spectra (Fig 2d). After extended ALE cycles, the Si 2p peak shifts to higher binding energy and it might indicate that SiO_x and SiF_x formed through the ALE cycles. The intensity of O increases and the intensity of N decreases along the ALE cycles. The fluorine signal was detectable and the signal in C 1s spectra was barely noticeable, which suggest fluorine remains after the ALE process and it combines with silicon in the process. The ellipsometry result (Fig 1) shows a consistent removal amount per cycle of 1.4 Å/cycle over the 20 ALE cycles.

11:40am PS1+MS+SS-FrM-11 Time Resolved Ion Energy Distribution in Pulsed Inductively Coupled Argon Plasma with/without DC Bias, Zhiying Chen, J. Blakeney, M. Carruth, P. Ventzek, Tokyo Electron America Inc.

Pulsed plasmas have emerged as promising candidates as means for precise control of ion energy/angle dependent surface processes and surface chemistry during plasma process, which are the key to 3nm and beyond device fabrication. The ion energy distribution functions (IEDFs) and ion fluxes over a pulsed period are important to understand as they directly influenced feature profile, damage and selectivity. We have developed an advanced plasma diagnostics (APD) system with advanced pulsing capability, including source, bias and synchronous pulsing. It is a compact inductively coupled plasma system with RF source frequency of 13.56 MHz intended to diagnose the general behavior of biased high-density plasmas. We report the effect of pulse frequency, RF duty cycle and power, DC duty cycle and voltage, and discharge pressure on the IEDFs and ion flux over a pulse period on the APD system. The time-resolved IEDFs and ion flux were measured using a retarding field energy analyzer. The ion energy transitions in a pulsed period from plasma ignition stage to stable stage and from plasma in glow period to afterglow period are studied. The results indicate the ion energy and ion flux are tailored by RF pulsing and RF-DC pulsing. The time-resolved IEDF demonstrates the merits of pulsing to precise control ion energy and flux, and the ion energy spread narrowed by pulsed plasma.

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 synergetic 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 synergetic 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 $c(2 \times 2)$ -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 $(4\sqrt{3} \times 4\sqrt{3})R30^\circ$ 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^{6-} 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 (GRazing incident Infrared absorption Spectroscopy Unit) 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

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passing through the first aperture (\varnothing 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (\varnothing 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 TiO₂(110)**, **Melissa Hines**, *W. DeBenedetti, Q. Zhu, M. Hasany, D. Somaratne*, Cornell University

Fluorine has been widely reported to improve the photoreactivity of TiO₂ 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 XeF₂ (g) at room temperature. The reaction initially produces a multi-nanometer-thick surface layer with a nominal composition of TiOF₂. The TiOF₂ layer largely dissolves with immersion in room temperature H₂O, 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 TiOF₂ 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 O₂ would be exoergic.

10:20am **SS1+AS+HC-FrM-7 Surface Structures of La_{0.8}Sr_{0.2}MnO₃ (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}MnO₃, 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 SrTiO₃ (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 VX (VX) on the clean and hydroxylated (101) surfaces of anatase titanium dioxide (TiO₂) 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

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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, $\text{NH}_4\text{Cl}(\text{aq})$, $\text{NaOH}(\text{aq})$, and $\text{NaOCl}(\text{aq})$. 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 Analogs During 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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