Surface Science
Room 209 CDE W - Session SS-MoA
Photo/Electrochemistry

Moderators: Rachael Farber, University of Kansas, **Liney Arnadottir**, Oregon State University

1:30pm **SS-MoA-1 Plasmonic Catalysis: Opportunities, Challenges, and Unresolved Questions***, **Suljo Linic**,* University of Michigan, USA **INVITED**

Metallic plasmonic nanostructures have emerged as an important class of optically active materials. The initial interest in these materials was based on their nano-antenna properties where these materials concentrate electromagnetic UV-vis fields in small volumes at the surface of the nanostructure. A critical problem with using these metallic materials as nano-antennas is that they lose a significant fraction of electromagnetic energy due to the formation of energetic electron-hole (e-h) pairs in the nanostructures.

There has been a growing realization that the formation of energetic charge carriers in the nanoparticles opens avenues for a number of applications including photocatalytic chemical conversion. At the core of these applications is the need to control the rate of formation of energetic e-h pairs, the location of their formation, and their flow in the nanostructure. There has been a high degree of interest in using hybrid nanostructures containing plasmonic nanoparticles, where the plasmonic component controls the interaction of light with the material, while the non-plasmonic component uses the resultant energetic carriers to perform a function. Examples of these materials include metal-metal, metal-semiconductor or metal-molecule hybrids. The use of these multicomponent materials introduces a number of fundamental questions related to the impact of the interface between the plasmonic and non-plasmonic component as well as the presence of the non-plasmonic material on the optical properties of the system, the flow of energy and excited charge carriers in the system.

I will discuss our work in the emerging field of hybrid plasmonic materials, focusing on the underlying physical principles that govern the flow of energy and excited charge carriers in these systems, as well as on common misconceptions and fundamental questions that deserve more attention and warrant additional studies.

References

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2:00pm **SS-MoA-3 Effects of Electric Fields and Solvents on the Surface Chemistry of Catalysis and Electrocatalysis***, **Charles T. Campbell**,* University of Washington

Understanding how liquid solvents affect the adsorption energies of catalytic reaction intermediates on transition metal surfaces, compared to their better-known values in gas phase, is crucial for understanding liquid-phase catalysis and electrocatalysis. For neutral adsorbates, the dominant effect is a decrease in adsorption energy compared to the gas phase by an amount equal to the solvents' adhesion energy to the solid multiplied by the surface area of the solid (that is blocked from solvent adsorption) per mole of adsorbed reactant. However, the electric field near the surface also has a strong effect on adsorption energies. When thermal catalytic or electrocatalytic reactions occur on metal surfaces in liquid solvents like water, an electrical double layer develops near the metal surface with a large electric field which changes with reaction conditions.This electric field affects the energies of adsorbed reaction intermediates and transition states, and therefore reaction rates. I will review ultrahigh vacuum (UHV) surface science studies regarding the effects of electric fields on the energies of adsorbed catalytic reaction intermediates, and show how these can guide predictions about how changes in electric fields from the double layer affect adsorbate energies on metal surfaces in liquids, and serve as benchmarks for validating accuracy of computational studies. In UHV, the electric field felt by an adsorbate can be strongly tuned by the addition of another adsorbed species nearby. Alkali adatoms exert a very strong change in electric field near the metal surface, which changes the energies of coadsorbed catalytic reaction intermediates, their electronic character and their reaction rates, as has been studied extensively in UHV. Assuming that changes in the field have only small effects on the strength of the weak attractions between adsorbate and solvent, the change in adsorbate energy with local electric field in a liquid is the same as in UHV. This approach explains the well-known observation that the binding energy of hydrogen adatoms (H_{ad}) to many late transition metal surfaces, as probed by cyclic voltammetry in water, increases with increasing pH. This change in H_{ad} energy in turn explains pH-induced changes in thermal catalytic and electrocatalytic hydrogenation reaction rates whereby H_{ad} must add to another species.

2:15pm **SS-MoA-4 In Air STM Observation of Au(111) Surface Disturbance Including Au Magic Fingers as Modified by Solvent Choice***, **Nazila Hamidi**, Erin Iski, Dillon Dodge, Rowan Dirks, Lauren Hornbrook,* University of Tulsa

The formation of Au magic fingers on Au(111) surfaces, a phenomenon first observed under "pristine" ultra-high vacuum (UHV) conditions, has long fascinated researchers due to its implications for nanoscale surface manipulation and quantum effects. This study explores the formation of these structures under more relevant conditions, specifically in air and at room temperature, using Scanning Tunneling Microscopy (STM). After exposing Au(111) to a 0.1 M solvent solution, three types of surface disturbances were observed, including the formation of Au magic fingers. The disturbance mechanism involved strong tip-surface interactions and the mass transport of Au atoms, influenced by the solvent choice. Various solvents, including $HClO_4$, HNO_3, HCl, NaOH, CH_2O_2, $CHCl_3$, C_5H_5N, and $C_2H_4O_2$, were tested for their effects on the surface disturbances. The degree of disturbance was categorized into significant & organized disturbance (SOD), significant & disorganized disturbance (SDD), and insignificant disturbance (IND).

The formation of Au magic fingers was primarily observed with solvents classified under SOD, such as $HClO_4$ and HNO_3, which facilitated the diffusion of Au atoms at a rate of 9.9 ± 1.1 nm^2/min. Solvents in the SDD category, like CH_2O_2, showed a diffusion rate of 4.0 ± 1.9 nm^2/min. Our findings reveal that the chemical properties of the solvent, particularly its total charge and electronegativity, play a pivotal role in modulating the surface dynamics of Au(111). The mechanism for the formation of Au magic fingers likely involved the adsorption of solvent molecules to the STM tip, which then picked up and moved Au atoms from the step edges to form nanowires. This study advances our understanding of solvent-surface interactions and demonstrates the potential for ambient STM to probe and manipulate nanostructures under practical, real-world conditions. The ability to form organized nanostructures like Au magic fingers in the air, without needing UHV or protective liquid layers opens new avenues for nanotechnology, catalysis, and surface chemistry applications. By bridging the gap between fundamental surface science and applied chemistry, this work underscores the importance of solvent choice in controlling nanoscale phenomena and paves the way for future innovations in nanomaterial design.

2:30pm **SS-MoA-5 Size-Selected Pt Clusters on N-Implanted HOPG: Oxygen Reduction Reaction and the Effect of Nitrogen Anchor Sites***, **Lokesh Saravanan**,* University of Utah*; Tsugunosuke Masubuchi,* Keio University, Japan*; Zihan Wang,* University of Utah*; Pavel Rublev, Yu Wei, Anastassia N Alexandrova,* University of California at Los Angeles*; Scott L Anderson,* University of Utah

Platinum clusters (Pt_n) have been considered as an effective electrocatalyst for the oxygen reduction reaction (ORR), the hydrogen evolution reaction and alcohol oxidation. In this work, atomically size-selected Pt_n were deposited under soft landing conditions (≤2 eV/atom) on indium tin oxide (ITO) and highly-oriented pyrolytic graphite (HOPG) electrodes in ultra-high vacuum, then studied electrochemically. The ORR activity exhibited strong substrate dependence, with Pt_n on HOPG showing up to a ~5 times increase in mass activity compared to Pt_n on ITO. However, clusters on pristine HOPG are unstable due to sintering, dissolution, and surface poisoning. To overcome the stability issue, nitrogen implantation has been employed to create anchoring sites on HOPG (N-HOPG). Pt_n deposited on N-HOPG showed improved stability against sintering and dissolution while retaining their high catalytic activity. The catalysts have been characterized by a combination of scanning tunneling microscopy (STM) and scanning transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) provided direct evidence of Pt-N interactions, revealing the nitrogen species that serve as chemically active binding sites. Density functional theory (DFT) calculations were performed to simulate both the cluster-surface interaction and the impact dynamics of N/N$_2$ ions during implantation. These simulations suggests that ion bombardment leads to penetration and modification of surface graphite layers, promoting the formation of anchor or defect-rich sites favorable for Pt$_n$ stabilization. These findings can provide fundamental insights into cluster stabilization mechanisms and the role of nitrogen anchoring sites on HOPG, offering a broader understanding of electrochemical transformations involving various metal clusters. I would like to acknowledge the support from the U.S. Department of Energy, Office of Science, under grant number DE-SC0020125.

2:45pm **SS-MoA-6 Surface Analysis of Planetary Regolith Particles: X-Ray Photoelectron Spectroscopy Results from the Asteroid Bennu***, **Catherine Dukes**, Lianis Reyes Rosa, Adam Woodson, Jackson Glass, Annabel Li,* University of Virginia*; Christopher Snead, Lindsay Keller,* NASA Johnson Space Center*; Michelle Thompson,* Purdue University*; Harold Connelly, Jr.,* Rowen University*; Dante Lauretta,* University of Arizona*; OSIRIS-REx Sample Analysis Team,* NASA

NASA's OSIRIS-REx mission to near-Earth primitive asteroid Bennu returned >120 grams of regolith. The rims of planetary regolith particles can exhibit a composition that is significantly different from the bulk, due either to geochemical processes on the parent body—such as interactions with aqueous environments—or to space weathering processes, including meteoritic impacts or solar wind irradiation. We investigate the surface composition of multiple Bennu particles from aggregate sample OREX-803205-0 via X-ray photoelectron spectroscopy (XPS). We compare these values with published bulk elemental abundances as well as energy-dispersive X-ray (EDS) spectroscopic measurements. XPS analyses were performed on a PHI Versaprobe III small spot instrument; SEM/EDS measurements were made with an FEI Quanta 650 with Oxford silicon drift detector.

The near-surface compositions of the >1 mm particles we analyzed are relatively homogeneous and comparable to the bulk elemental content [1], containing Mg, Si, O, Na, Fe, S, Al, Cr, Mn, C, Cl, and F [2]. The Bennu particle surfaces exhibit lower carbon and oxygen signatures (C: 11–13.4 at-%, O: 56–60 at-%) than the Murchison meteorite surfacial concentrations (C: 16–19 at-%, O: 60–64 at-%) — presumably the result of controlled sample handling and/or indicative of space weathering [3]. The surface abundances of Na (0.6–2.8 at-%), Mg (10.1–13.4 at-%), and Si (10.1–11.9 at-%) are significantly greater for Bennu than Murchison, where <<1 at-% Na has been observed and Mg content is only 3–5 at-% [3]. No Ca was observed on the Bennu particle rims, which is surprising because ICP-MS bulk analysis identifies Ca at concentrations similar to Na [1]. These differences may be the result of sample inhomogeneities, but are most probably indicators of aqueous exposure.

The <1 mm Bennu regolith particles that we analyzed have surface constituents identical to those of the >1 mm particles but exhibit more compositional variation. In particular, S (to 2.1%) and Na (to 3.8%) are highly enriched on some particles. Na enrichment may have originated from salty precipitates generated by a subsurface brine within Bennu's parent body [4], such exposure can also preferentially leach elements such as calcium from particle rims [5].

Acknowledgments: This material is based upon work supported by under contract no. NNM10AA11C issued through the New Frontiers Program.

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3:00pm **SS-MoA-7 X-Ray Photoelectron Spectroscopy informs on Hybrid Photoelectrode Surface Passivation and Durability***, **Jillian Dempsey**,* University of North Carolina at Chapel Hill **INVITED**

Integration of CO$_2$ reduction molecular catalysts with silicon photoelectrodes can be achieved through covalent attachment methods, such as hydrosilylation, where hydrogen-terminated silicon is reacted to form silicon-carbon bonds. These hybrid photoelectrodes use sunlight to drive the conversion of CO$_2$ to value added fuels and chemicals. Incomplete reaction of the atop silicon sites can leave reactive sites that are prone to corrosion and lead to the formation of defects that trap photogenerated carriers. X-ray photoelectron spectroscopy provides critical information both on the success of the catalyst attachment, as well as the extent of passivation through detection of SiO$_2$ growth. Further, XP spectra recorded before and after controlled potential photoelectrolysis inform on the durability of the covalently modified silicon surface and guide the development of improved hybrid photoelectrodes.

4:00pm **SS-MoA-11 Investigation of the Interaction between Water Vapor and Ni Nanoparticles Supported Over Ceria***, Nishan Paudyal, Erik Peterson, Yinghui Zhou,* University of Wyoming*; Sanjaya Senanayake,* Brookhaven National Laboratory*; **Jing Zhou**[1],* University of Wyoming

Understanding the role of water vapor in the growth and sintering of ceria-supported Ni nanoparticles is important since it can provide insights into their promising activity towards reactions in which water is a key reactant. In our study, we prepared fully oxidized CeO$_2$(111) and partially reduced CeO$_{1.75}$(111) thin films as model catalytic supports for Ni and studied the detailed nucleation, size, and distribution of Ni nanoparticles under ultrahigh vacuum (UHV) conditions using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Deposition of Ni with submonolayer coverages at 300 K produces small particles that are uniformly distributed over both oxidized and reduced ceria surfaces. The particles agglomerate into large three-dimensional features that are on average 1.0 nm high after heating to 700 K. Furthermore, the particles show a clear preferential decoration at step edges on CeO$_2$ due to enhanced diffusion at elevated temperatures. The Ni particle growth with heating was also observed over reduced ceria. However, due to a stronger interaction between Ni and reduced ceria with defects (e.g. oxygen vacancies/Ce^{3+}), smaller Ni particles are formed over CeO$_{1.75}$. Exposure of water vapor to the Ni/ceria surface at 300 K can influence the sintering behavior of Ni, causing the formation of significantly flatter particles with heating compared to Ni over adsorbate-free ceria that are attributed to unique adsorbate-metal-oxide interactions. We also conducted the experiments when water was first dosed onto ceria supports followed by subsequent Ni deposition at 300 K. Surface defects (e.g. oxygen vacancies) over reduced ceria are the active sites for water dissociation to form hydroxyl groups at 300 K. This creates fewer nucleation sites for Ni upon deposition over CeO$_{1.75}$ at room temperatures and an extensive decrease in its particle density. Predosed water over CeO$_{1.75}$ also causes significant sintering of Ni nanoparticles with subsequent heating to higher temperatures. Our experimental findings suggest distinct adsorbate-metal-oxide interactions are key to tune the properties of Ni nanoparticles over reducible CeO$_x$(111) surfaces caused by water exposure. Such interactions are essential in consideration for further modification of Ni-based catalysts for improved reactivity and stability.

4:15pm **SS-MoA-12 The Effect of Surface Reaction Intermediates on the Interaction of Solvent Molecules with Pt(111) Model Catalyst***, **Valeria Chesnyak**,* Oregon State University*; Arjan Saha,* Washington State University*; Marcus Sharp,* University of Washington*; Zbynek Novotny,* Pacific Northwest National Laboratory*; Nida Janulaitis, Charles T. Campbell,* University of Washington*; Zdenek Dohnalek,* Pacific Northwest National Laboratory*; Liney Arnadottir,* Oregon State University

The interaction energies of molecules with solvents on metal surfaces contribute to processes in heterogeneous catalysis and electrocatalysis. Such interactions are essential in catalytic biomass conversion reactions, pollution cleanup, and energy transition. The impact of solvents on the adsorption energetics of reactants, reaction intermediates, and transition states determines reaction rates and selectivity. While adsorption enthalpies of many reactants on metal surfaces in vacuum have been reported, how they change in the presence of liquids remains poorly understood.[1] Computational methods such as density functional theory (DFT) can predict adsorption energies, including coadsorption and solvation effects at the reactant-solvent-catalyst interface. However, these models require experimental benchmarks for validation, as significant discrepancies persist between calculated and experimental adsorption enthalpies. We present here results aimed to provide such benchmarks for the interaction energies between adsorbed intermediates and solvents on metal surfaces.

Single Crystal Adsorption Calorimetry (SCAC) is the only technique capable of directly measuring the molecular and dissociative enthalpies of adsorption on well-ordered single crystalline surfaces. We employ a state-of-the-art microcalorimeter, developed by the Campbell group,[2] to understand coadsorption-induced effects of common agents in catalysis on surfaces. Specifically, we measure the differential heats of adsorption for water and methanol coadsorbed with CO or hydrogen on clean Pt(111). On Pt(111), CO forms a $\sqrt{3}\times\sqrt{3}$ R30° structure, while molecular hydrogen dissociates to form a (1×1) hydrogen atom adlayer at cryogenic

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[1] **JVST Highlighted Talk**

temperatures (100 K). Understanding the effects of these pre-adsorbed catalytic intermediates on the adsorption energies of the solvents provides important benchmarks for validating computational models.

References:

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4:30pm **SS-MoA-13 Mechanistic Insights into C–C Bond Formation in Photoinduced and Photocatalytic Reactions on Reducible and Non-Reducible Oxide Surfaces***, Aakash Gupta,* University of Central Fllorida*; Keith Blackman, Eric Segrest,* ***Mihai Vaida,*** University of Central Florida

The formation of carbon–carbon (C–C) bonds is a fundamental step in numerous catalytic processes that drive the synthesis of diverse materials, including commodity chemicals, polymers, cosmetics, and pharmaceuticals. Understanding how C–C bonds are created in heterogeneous reactions at the gas–solid interface, and how this process depends on the properties of the solid surface, is essential for improving the efficiency of these reactions.

This study examines the transformation of single-carbon species into two-carbon species through the coupling of CH_3 radicals and tracks the subsequent evolution of these intermediates on various oxide surfaces. The investigation employs an experimental strategy that integrates time-of-flight mass spectrometry with pump–probe spectroscopy, along with rapid preparation of the surface with molecules.

On irreducible oxide surfaces such as silicon oxide, the reaction is initiated by a pump laser pulse at a central wavelength of 266 nm. This pulse excites the CH_3I precursor molecules into the dissociative A-band, resulting in the formation of CH_3 and I fragments. A subsequent probe laser pulse in the ultraviolet range ionizes the reaction intermediates and final products, which are then detected and analyzed using time-of-flight mass spectrometry. Alongside bimolecular processes that yield I_2 and regenerate CH_3I, the formation of C_2H_6 can be monitored with femtosecond resolution.

On reducible metal oxide surfaces, including TiO_2(110) and amorphous TiO_2, the reaction pathway is more complex and extends over considerably longer timescales. In the case of TiO_2(110), the process begins with photodissociation of adsorbed CH_3I precursor molecules. The resulting CH_3 radicals can couple on the surface to produce C_2H_6, which subsequently undergoes photocatalytic oxidative dehydrogenation to form C_2H_5, C_2H_4, and H_2O. An additional reaction channel involves dehydrogenation of surface-adsorbed CH_3 radicals, leading to the generation of CH_2 species. On amorphous TiO_2 surfaces, however, C–C bond formation predominantly proceeds through dissociative adsorption of CH_3I molecules.

Such investigations provide detailed insights into C–C bond formation across a variety of surfaces and precursors, offering new opportunities to understand and control surface reactions of significant industrial and technological relevance.

4:45pm **SS-MoA-14 Studying the Intermolecular Forces That Drive Magic Number Clustering***,* ***Alex Walter****, S. Alex Kandel,* University of Notre Dame

The intermolecular forces that drive crystallization also drive cluster formation in solution. These clusters can be measured using electrospray ionization mass spectrometry (ESI-MS) as the soft ionization technique does not break up supramolecular clustering, and the information can be used to study pathways to bulk crystallization. Clusters that appear at higher frequencies than would be expected are called magic number clusters and have highly favorable geometries, charge distributions, or energies. In a solution together, guanine and cytosine form magic number tetramers (3:1 guanine: cytosine). During MS/MS experiments, the tetramers break into guanine dimers and 1:1 guanine: cytosine clusters. This is not the expected Watson-Crick binding pattern, but rather a Hoogsteen binding pattern where the N7 purine and the C4 amino group are binding to the N3 and C4 positions of the other guanine. Replacing a guanine with a cytosine stretches this geometry. Substituting the guanines with 9-methylguanine shows the same binding pattern, as the N9 position does not participate in the Hoogsteen binding, but replacing the guanines with 6-O-methylguanine breaks this clustering entirely as the methyl group sterically blocks magic number cluster formation. This technique is applied to other systems, including melamine with cyanuric acid and adenine with thymine/uracil to learn more about magic number clustering, the intermolecular forces that drive solution assembly, and crystallization.

5:00pm **SS-MoA-15 Application of XPS to Detect Low-Energy Electron (1–25 eV) Irradiation-Induced DNA Degradation***,* ***Hao Yu,*** University of Notre Dame*; João Pereira-da-Silva,* Universidade NOVA de Lisboa, Portugal*; Jackson King, Thejaswini Basappa, Bo-An Chen, Pitambar Sapkota,* University of Notre Dame*; Filipe Ferreira da Silva,* Universidade NOVA de Lisboa, Portugal*; Sylwia Ptasińska,* University of Notre Dame

Low-energy electrons (LEEs, typically 1–30 eV) are known to induce DNA damage through surface-localized interactions occurring within only a few nanometers of depth, primarily via dissociative electron attachment (DEA). These processes can lead to localized bond scission and chemical modifications in specific molecular components. To examine these changes, we employed X-ray Photoelectron Spectroscopy (XPS). In this study, we investigated various components of DNA irradiated with LEEs in the 1–25 eV range, using XPS to monitor energy-dependent chemical modifications.

The investigated targets included double-stranded calf thymus DNA and plasmid DNA (pUC18), as well as four nucleosides together with their corresponding nucleobases, representing eukaryotic DNA, prokaryotic DNA, and individual base components, respectively. Samples were deposited on substrates to form dry thin films for surface analysis. The films were then irradiated with LEEs for durations ranging from 30 minutes to 8 hours under ultrahigh vacuum conditions (base pressure ~2 × 10^{-10} mbar). XPS measurements using an Al Kα X-ray source (70–100 W), focusing on the O 1s, C 1s, N 1s, and P 2p core levels, were performed both during and after irradiation under the same UHV conditions.

At 5 and 10 eV, DNA undergoes core-excited dissociative electron attachment (DEA), and we observed selective cleavage of C–N (N-glycosidic) and C–O bonds in plasmid DNA. Damage patterns at these energies were similar, with the extent of modification increasing progressively with irradiation time. In contrast, at 1 eV, where shape-resonant DEA dominates, chemical modifications were minimal, consistent with the limited effectiveness of DEA at such low energies. The TE buffer remained stable under extended X-ray and LEE exposure, but appeared to enhance the yield of site-selective DNA damage under LEE irradiation. At 25 eV, LEEs promoted DNA degradation through combined ionization and DEA pathways. Analysis of calf thymus DNA showed evidence consistent with cleavage of C–O and C–N bonds and disruption of the phosphate backbone. Comparison among four nucleosides revealed that thymidine and guanosine exhibited the most pronounced spectral changes, while cytidine and adenosine were more resistant. Additionally, nucleosides were more susceptible to electron-induced damage than their corresponding nucleobases, indicating that LEEs may preferentially target sugar moieties and N-glycosidic bonds.

5:15pm **SS-MoA-16 Unmasking Local Phenomena in Electrochemistry through Scanning Electrochemical Cell Microscopy***,* ***Miguel Bernal****, Dario Stacchiola,* Center for Functional Nanomaterials, BNL

Electrochemical reactions at solid–liquid interfaces are at the heart of catalysis, energy conversion, and materials durability. However, the traditional way we study them—using electrodes with macroscopic dimensions—tends to blur the picture. Averaging over large surfaces hides the fact that many processes, from the nucleation of a nanoparticle to its eventual dissolution, actually take place in a highly heterogeneous and stochastic manner at the micro- and nanoscale.

In our work, we use scanning electrochemical cell microscopy (SECCM) to confine the electrochemical reaction to tiny, micrometer- and submicrometer-sized regions of interest. This localized probing allows us to capture electrochemical “snapshots” that reveal just how variable processes such as metal nanoparticle growth and dissolution can be from one spot to the next.

By examining hundreds of such localized measurements, we can build statistical maps of activity across a surface, linking electrochemical behavior with substrate heterogeneity and particle-scale transformations. Even more insight emerges when SECCM is combined with complementary high-resolution imaging, such as in-situ electrochemical transmission electron microscopy (EC-TEM), which directly visualizes dissolution one nanoparticle at a time.

Taken together, these approaches show that electrochemical reactivity is not uniform but intrinsically local and dynamic. Understanding this hidden complexity opens new opportunities for the design of durable electrocatalysts and functional nanomaterials, where performance and stability hinge on events occurring at the level of single entities. Local electrochemical probing thus provides a powerful lens to bridge the gap between ensemble electrochemistry and the reality of nanoscale processes.

Surface Science
Room 209 CDE W - Session SS+2D-TuM

Complex Phenomena on Surfaces

Moderators: Te-Yu Chien, University of Wyoming, **Bo-Hong Liu**, National Synchrotron Radiation Research Center

8:00am **SS+2D-TuM-1 Atomically Precise Synthesis and Characterization of Defect Structures in Graphene*, An-Ping Li,*** Oak Ridge National Laboratory **INVITED**

Atomically precise engineering of defects and interfaces in graphene, along with a detailed understanding of its structure-dependent electronic properties, is essential for the advancement of graphene-based quantum electronic applications. Here we present recent progress in the controlled synthesis and atomic-resolution characterization of defect structures in graphitic nanomaterials. The first approach involves bottom-up synthesis of graphitic nanostructures using on-surface chemical reactions using rationally designed molecular precursors. Particularly, graphene nanoribbons (GNRs) are obtained on a non-metallic substrate, showing entangled magnetic states that are decoupled from the substrate. The multistep thermally triggered transformations rely on highly selective and sequential activations of C-Br, C-F bonds, followed by cyclodehydrogenation. Scanning tunneling microscopy and spectroscopy (STM/S) are used to monitor the formation of intermediates and GNRs, revealing a weak interaction between GNRs and the substrate. The second approach employs a top-down strategy to introduce oxygen (O) substitutions into epitaxial graphene grown on SiC. Techniques including ion implantation and STM tip-assisted manipulation are used to create sp^2-hybridized O dopants and control its configuration. A combination of chemical-bond-resolved non-contact atomic force microscopy (ncAFM) and STM is used to investigate the structural and electronic properties of the O-related defects. The STM/S measurements, supported by DFT calculations, indicate that the sp^2-hybridized O dopant hosts a characteristicπ-orbital electronic state below the Dirac point. Tuning the Fermi level with electric field may achieve single-electron occupancy of these atomically defined centers. Such control opens the door to the realization of long coherence electron-spin qubits, providing pathway toward graphene-based quantum technologies.

The research was conducted at the Center for Nanophase Materials Sciences (CNMS), a US Department of Energy User Facility.

8:30am **SS+2D-TuM-3 Fabrication of Graphene Nanoribbons/Organic Molecules Interface*, A.M. Shashika D. Wijerathna,*** *Markus Zirnheld,* Old Dominion University*; He Zhao,* Central South University, China*; Rockwell Li,* Old Dominion University*; Pingshan Wang,* Central South University and Guangzhou University, China*; Yiming Li,* Central South University, China*; Yuan Zhang,* Old Dominion University

Graphene derivative materials are great superlubricant candidates that can be potentially utilized in molecular devices. Therefore, it is essential to understand the mechanical property at the interface that is formed by organic molecules and graphene derivatives materials. In this study, we fabricated an interface formed by organic molecules with armchair graphene nanoribbons and studied its mechanical properties.

15-carbon-wide armchair graphene nanoribbons (15-AGNRs) were synthesized on Au(111) substrate in a bottom-up approach with dibromo-p-pentaphenyl (DBPPP) as precursor molecules. Precursor molecules, DBPPP exhibit two different self-assembly patterns on Au(111) substrate, forming rectangular domains and hexagonal domains. Both self-assembly structures can be successfully transformed into 15-AGNRs through polymerization at 370 K and, subsequently, cyclodehydrogenation at 470 K. 30-GNRs were also observed in some cases.

Subsequently, pentacene molecules, a linear polycyclic aromatic hydrocarbon consisting of five linearly-fused benzene (C_6H_6) rings, were deposited onto the AGNRs to form the interface pentacene/AGNRs. Pentacene molecules exhibited a preference for adsorption on the Au(111) substrate than the graphene nanoribbons. Therefore, they first fill in gapping areas formed in between graphene nanoribbons, and once the metallic surface sites are fully occupied, they adsorb onto the ribbons. Pentacene is adsorbed on AGNRs in different orientations, which include nearly transverse, oblique, and nearly axial. Among these, the most energetically favorable and stable orientation is nearly transverse, where the pentacene molecular long axis is approximately 93° clockwise relative to the GNR axis. Notably, external mechanical energy facilitated the movement of pentacene molecules along the GNRs, suggesting low molecular-scale friction. These findings provide critical insights into the adsorption behavior of pentacene on AGNRs and mechanical properties of the interface, which is essential for advancing their applications in organic electronics.

This work is conducted with a low-temperature (~77 K), ultra-high vacuum (10^{-10} mbar) scanning tunneling microscopy (LT-UHV-STM).

Keywords: Armchair Graphene Nanoribbons, Pentacene, Friction at Molecular Interface, Adsorption Orientation, Scanning Tunneling Microscope

8:45am **SS+2D-TuM-4 Visualizing the Products of Scattering at Surfaces: Hot Transient Motion of N on Ru(0001) and Coverage Dependent Mobility and Placement of O on Moiré Graphene*, Joshua Wagner*[1,2]***, *Steven Sibener,* University of Chicago

Diffusion of atomic species is a pivotal process in surface chemistry for topics ranging from catalysis to material stability. This presentation focuses on two types of atomic mobility: the nonthermalized "hot" atomic motion of N atoms following dissociative chemisorption of N_2 and the highly correlated coverage-dependent diffusion of oxygen atoms on moiré patterned graphene. Overall, results provide spatially rich and atomically resolved insight to on-surface dynamics and illustrate a new direction in the study of interfacial reaction dynamics where outcomes such as site-specific reactivity and non-thermalized diffusion can be examined using incident kinetic energy and angle of incidence as reaction control parameters.

Ruthenium based materials serve as more energy efficient catalysts for the dissociative chemisorption of N_2, the rate limiting step of ammonia synthesis *via* the Haber-Bosch process. Despite the global importance of this chemical process, open questions remain concerning the dissipation of energy following dissociation. Answering these questions may inform catalyst design and will enrich our understanding of fundamental surface dynamics.

To probe the energy dissipation pathways of N_2 dissociation on Ru(0001), tight control of the energy and angle of incident N_2 is achieved *via* supersonic molecular beam fluxes of N_2 molecules. An in-line and *in situ* scanning tunneling microscope (STM) provides atomic-scale visualization of surface products. Analysis of the spatial distributions of N adatoms from the same molecule as a function of incident energy and angle provides insight to the energy dissipation pathways such as energy transfer to phonons and electron hole-pair excitations following dissociative chemisorption.

Exchanging a resistively heated pinhole nozzle for an RF plasma source, the molecular beam can also deliver supersonic ground state atomic oxygen. The site-specificity of atomic oxygen binding on the graphene-Ru(0001) moiré lattice is shown here to be coverage dependent. Furthermore, the stability of oxygen species on epitaxial graphene varies with the number of proximal O atoms as shown by STM imaging. Effects of multiparticle interactions appear in pair-distribution functions, oxygen binding distributions on the moiré lattice, and the diffusivity of O atoms. Comparison of monolayer versus bilayer graphene additionally demonstrates the role that spin-flipping dynamics play in the adsorption of O(^{3}P) on graphitic surfaces. Overall, results provide insight to the stability of moiré-patterned two-dimensional materials which show promise as platforms for next-generation quantum materials and catalysts.

9:00am **SS+2D-TuM-5 Oxygen Diffusion Dynamics on a Rh(111)/(322) Multifaceted Surface*, Alexis Gonzalez,*** *Elizabeth Serna-Sanchez, Maxwell Gillum, Stephanie Danahey, Dan Killelea,* Loyola University Chicago

The diffusion of oxygen on multifaceted Rhodium (Rh) crystals is of significant interest due to the importance of Rh in heterogeneously catalyzed reactions, such as surface-facilitated oxidation reactions. In this study, we investigate the diffusion dynamics and oxygen species on these two surfaces using temperature-programmed desorption (TPD) and low-energy electron diffraction (LEED) techniques. Despite the structural differences between the (111) and (322) facets, our experiments reveal that the oxygen species on both surfaces are similar, with oxygen existing on the surface as atomic oxygen shortly after adsorption. TPD experiments show that oxygen desorption occurs at comparable temperatures on both surfaces, indicating similar binding energies for oxygen species on each facet. However, LEED shows that there may be different structures forming on either side of the crystal and the orientation of oxygen species are

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[1] **AVS Dorothy M. and Earl S. Hoffman Awardee**

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

dissimilar. These findings suggest that the oxygen species formed on both (111) and (322) surfaces are essentially the same even though the two surfaces have different atomic arrangements. This observation highlights the importance of other factors, such as surface defects and temperature, in governing the oxygen diffusion process. The study provides information on how surface structure influences the diffusion behavior of oxygen on Rh crystals and emphasizes the need for considering both surface morphology and adsorption characteristics in the design of catalytic materials.

9:15am **SS+2D-TuM-6 CO Adsorption on Gr/Ni(111) Single Point Defects***, **Francesco Armillotta**[1],* EPFL, Switzerland

Single atom catalysis (SAC) has attracted great interest due to its potential high selectivity, reduced material consumption, and activity. However, a detailed atomistic insight into the active sites and reaction details is still limited, which is fundamental for the understanding and engineering of SAC. We show that even simple molecular adsorption and desorption can reveal non-trivial aspects that affect, for example, the overall sticking probability. We study the CO chemisorption on a model single atom catalyst, where single Co and Ni atoms are adsorbed (or stabilized) in graphene (Gr) vacancies during graphene growth by chemical vapor deposition (CVD) on a Ni single crystal.[1,2]The study is carried out using a custom designed high-resolution Thermal Desorption Spectroscopy (TDS) instrument in combination with a Variable Temperature STM. In particular, the TDS instrument allows for the study of active sites with a very low surface coverage, of the order of 10^{-3} monolayers. We provide a thorough characterization of the active sites for CO adsorption on Gr (Fig. 1a).[3,5] In particular, the identification of Ni and Co in Gr di- and tri-vacancies, the dependence on the azimuthal Gr orientation, and an unreported CO chemisorbed state on pristine Gr. We show that the nature of the single point defect can have a huge impact on the CO adsorption probability, accounting for differences up to a factor of 10^4. We explain the existence of very different main adsorption channels, such as a reverse spillover (Fig. 1b) and activated adsorption *via* a precursor state (Fig. 1c), both known for extended surfaces but never reported for single atoms.[4,5] The well-defined geometries allow for direct and reliable comparison with *ab initio* simulations, revealing important thermodynamic and kinetic aspects.

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9:30am **SS+2D-TuM-7 Spin and Transport in Graphene Nanostructures with π-Magnetism***, **Thomas Frederiksen,*** Donostia International Physics Center (DIPC), Spain **INVITED**

The emergence of π-magnetism in open-shell graphene nanostructures—long anticipated from theoretical models—has seen remarkable experimental breakthroughs in recent years, driven by advances in on-surface synthesis and scanning probe techniques. These developments have enabled the realization and manipulation of localized spin states with atomic precision, opening new opportunities in spin-dependent phenomena at the nanoscale. In this talk, I will highlight recent progress in understanding and engineering π-magnetism in graphene nanostructures through three complementary theoretical perspectives. First, I will discuss theoretical efforts to interpret scanning tunneling microscopy (STM) experiments that probe spin-resolved phenomena in atomically precise nanographenes. Second, I will present theoretical results on hyperfine interactions in π-magnetic nanographenes, where significant and anisotropic couplings suggest promising avenues for detection via techniques such as ESR-STM and for studying coherent nuclear dynamics. Finally, I will introduce a proposal for a spin-polarizing electron beam splitter based on crossed graphene nanoribbons, showing how such structures could serve as building blocks for spintronics and quantum interference devices. Together, these directions underscore the potential of graphene nanostructures for both fundamental quantum science and future quantum technologies.

11:00am **SS+2D-TuM-13 Simultenous Electron Spectroscopy and X-Ray Scattering on Model Ceria Catalysts***, **Baran Eren,*** Weizmann Institute of Science, Israel **INVITED**

Heterogeneous catalysis is a timely and critical research field in basic and applied energy sciences, due to its potential to provide solutions to global environmental issues. However, there is still a lack of a profound understanding of the molecular and structural processes at the interfaces between solids and reactant gases. A detailed understanding of the correlation between the chemistry, structure, and function in these materials requires a multimodal investigation. Over the past few years, scientists at the at the Advanced Light Source, the Berkeley synchrotron facility, have developed a unique setup attached to an X-ray beamline where chemically-sensitive ambient pressure X-ray photoelectron spectroscopy (APXPS) and structure-sensitive grazing incidence X-ray scattering (GIXS) experiments can be performed simultaneously. Here, we showcase that this tool can provide mechanistic insights that are unparalleled in the literature.

This novel approach allows us to probe the changing surface and bulk chemistry, and surface and bulk structure of the model ceria catalysts in the presence of H_2 and CO_2 gases. In addition to the method itself, the electron density, surface chemistry, and roughness trends observed in ceria during the reaction will be discussed in this talk.Access to such a variety of data from working catalysts in a single experiment can have far-reaching implications, because changes in surface roughness, ability to store hydrogen in the bulk in various forms, and the chemical state of the surface, which all depend on the reactive environment, can directly affect the catalyst performance.

11:30am **SS+2D-TuM-15 Vibrational Spectroscopic Identification of Carbon Absorbed Beneath the Metal Surface***, **Santosh K. Singh**[2], Volkan Cinar, Sylvia T. Ceyer,* Massachusetts Institute of Technology

Carbon dissolved in transition metals, also known as subsurface or bulk carbon, plays a critically important role in many technological processes. Subsurface carbon atoms have been recognized as essential for the catalytic growth of carbon nanotubes, graphene synthesis, and operation of direct carbon fuel cells. Despite the recognition of carbon bound beneath the surface of a metal as a crucial species in many chemical and catalytic processes, it has not been identified spectroscopically using methods that do not destroy the sample. We report the first vibrational spectroscopic identification of bulk carbon in a Au-Ni(111) surface alloy by high-resolution electron energy loss spectroscopy (HREELS) and its unambiguous synthesis via collision-induced absorption (CIA). The vibrational modes of carbon embedded beneath the surface alloy are shown to be distinguishable from surface-bound carbon based on their intensity dependence on the incident electron energy. Three distinct peak features, centered around 690, 500, and 380 cm^{-1}, are assigned to modes of subsurface carbon atoms that are located at octahedral sites and triangular misfit dislocation loops of the second layer of Au/Ni surface alloy. Additional confirmation of these assignments come from their appearance after CIA experiments, in which surface bound carbon atoms are hammered into the bulk by collisions with energetic gas phase Xe atoms, accompanied by a decreased intensity of the surface carbon mode at 540 cm^{-1}.This work reports for the first time a new method to spectroscopically identify interstitial carbon below the surface of a solid metal and a non-thermal method to synthesize it.

11:45am **SS+2D-TuM-16 Pt-Sn Catalysts for Selective Hydrogenation of Furfural***, **Donna Chen**, Sharfa Farzandh,* University of South Carolina*; Wenrui Chai, Katherine Mader, Graeme Henkelman,* University of Texas at Austin*; Mengxiong Qiao,* University of South Carolina

The production of high value chemicals from biomass is an attractive option for reducing economic dependence on fossil fuels, and the development of new catalysts for selective transformation of highly functionalized biomass derivatives has become an important area of research. For example, furfural is a platform chemical derived from biomass reforming, and catalysts are needed for the desired selective hydrogenation of furfural to furfuryl alcohol, which is a high-value chemical used in adhesives, resins, and coatings. In this work, model Pt-Sn surface alloy catalysts were prepared in ultrahigh vacuum (UHV) by vapor-depositing Sn on Pt(111) and annealing to various temperatures. Specifically, a $\sqrt{3}$x$\sqrt{3}$-R30 low energy electron diffraction pattern was observed after annealing one monolayer of

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

Sn on Pt(111) to 800 K, while a p(2x2) pattern was observed after annealing to 1000 K. Low energy ion scattering studies confirmed that these two ordered overlayers have compositions roughly corresponding to Pt_2Sn and Pt_3Sn, respectively. Furfural hydrogenation was studied in a microreactor coupled directly to the UHV chamber under reaction conditions of 0.1% furfural/balance H_2 at 160 ºC. On Pt(111), conversion was low (~5%), with THF and furan as the main products and no furfuryl alcohol produced.However, on the p(2x2) surface, the desired furfuryl alcohol product was formed with ~70% selectivity, and conversion was ten times higher than on Pt(111). Furfuryl alcohol was also observed on the √3x√3-R30 alloy surface, but the yield was only 25% of that on the p(2x2) surface. Furthermore, furfuryl alcohol production was even lower on annealed Pt-Sn surfaces with lower Sn coverages or unannealed surfaces with the same coverage. Density functional theory and minimum energy pathway calculations showed that in the first hydrogenation step, hydrogenation at the carbonyl oxygen is both kinetically and thermodynamically favored on the Pt, Pt_3Sn, and Pt_2Sn surfaces. In the second step, hydrogenation at the C-OH carbon has a low energy barrier (0.3 eV) on the Pt_3Sn surface but is not favorable on Pt(111) or Pt_2Sn ($\geq$0.8 eV). These differences are explained by a combination of electronic effects that decrease the binding energy of hydrogen on the Pt-Sn alloy surface and adsorption geometries. Furfural hydrogenation was also studied on bimetallic Pt-Sn clusters supported on TiO_2(110), but these surfaces were always rich in Sn and not active for furfuryl alcohol formation.

12:00pm **SS+2D-TuM-17 Bimodal Sputter Depletion of Adsorbed Na from Granular, Regolith-Like, Olivine Targets***, **Adam Woodson**, Cassandre Morel, Noah Jäggi, Catherine Dukes,* University of Virginia

Regolith roughness is expected to modulate the sputter flux of surface atoms into the exospheres of airless bodies such as Mercury. Studies have shown that roughness—from the nanometer scale upward—promotes redeposition and diminishes total sputtering yields. Experiments involving irradiation of minerals and single-element powders demonstrate yield reductions anywhere from 15% to 70% as compared to smooth targets, but the grain size dependence of this effect has not been adequately parameterized. Understanding this mechanism is therefore of critical importance for quantifying desorption and sputter ejection and for predicting the relative contributions of release processes from planetary surfaces.

We measured the sputter depletion of adsorbed Na from polished natural olivine and from synthetic granular forsterite targets with narrow grain size distributions from 45 µm up to 520 µm. Na vapor was deposited onto each target in an ultrahigh vacuum system and then irradiated at either 15° or 60° incidence (from global surface normal) to prescribed fluence steps using 4 keV He^+ ions. All experimental steps were carried out at room temperature (~300 K). After each fluence step an XPS spectrum was acquired and used to quantify the remaining Na surface concentration. Depletion cross sections were then extracted from the concentration vs. fluence data for each target, and sputtering simulations were conducted using SDTrimSP to recreate experimental observations and corroborate target surface structure and stoichiometry.

For the polished targets, Na concentrations exhibited single-exponential decay with increasing fluence, and depletion at 60° incidence outpaced that at 15° as expected from theory. Conversely, for all granular samples the Na concentrations exhibited at least double-exponential decay and depletion occurred more quickly at 15°. We propose that this reflects faster removal of Na that is directly exposed to the incident ion flux, convolved with slower removal of shadowed Na by—primarily—reflected incident ions. We found that the shadowed sodium was sputtered away 10–100 times more slowly than the exposed Na, with a transition from single-exponential to double-exponential decay at some threshold between nanoscale roughness (polished targets) and microscale roughness. These results may help to explain, for example, why current models underestimate the persistence of Na density enhancements in Mercury's dayside exosphere, as observed by the MESSENGER spacecraft's UltraViolet and Visible Spectrometer.

Surface Science
Room 209 CDE W - Session SS-TuA
Heterogeneous Catalysis I

Moderators: Zbynek Novotny, Paul Scherrer Institute, Switzerland, **Dario Stacchiola**, Brookhaven National Laboratory

2:15pm **SS-TuA-1 Interstellar Catalysis - a Route to Molecular Complexity in Space***, **Liv Hornekaer,*** Aarhus University, Denmark **INVITED**

Interstellar molecular clouds, the regions where new stars and planetary systems form, are home to surprisingly complex chemistry. In spite of the very low temperatures and pressures characterizing these clouds more, than 330 different molecules have so far been detected. Nanoscale interstellar dust grains and polycyclic aromatic hydrocarbons are expected to play a dominant role as catalysts for the low temperature reactions resulting in the formation of these molecules. Their catalytic effect is not only ascribed to a lowering of reaction barriers, but also to their role in dissipating the energy released in the reaction. In some cases, the "catalysts" are even seen to increase the reaction barriers, while still enabling the reaction to proceed by providing energy dissipation pathways. The last 20 years have seen major advancements in our understanding of interstellar reactions, specifically with regards to simple molecules, however, the degree of chemical complexity attainable via such reactions is still under exploration. Recently it was shown that the simplest amino acid, glycine, can form under interstellar conditions. In this case a non-diffusive reaction mechanism was proposed. A more detailed quantum dynamical understanding of low temperature solid state radical-radical reactions could provide the answer to the question of whether the molecular building blocks of life – amino acids, DNA bases, sugars and fatty acids – can form in interstellar space, even before the formation of stars and planets. To answer this question, we recreate interstellar conditions in the laboratory and employ the full toolbox of surface science to study heterogenous catalytic reactions on interstellar dust grain analogue surfaces. As an example scanning tunneling microscopy measurements allows us to directly image low temperature ice cluster formation, as well as low temperature reaction products with single molecule detection efficiency.

2:45pm **SS-TuA-3 Kinetics and Dynamics of CO Oxidation on Rhodium Surfaces***, **Dan Killelea,*** Loyola University Chicago

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of the CO oxidation reaction and subsurface emergence.

I will discuss our observations of CO oxidation by co-adsorbed and absorbed oxygen on Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, the role of systematic defects will be covered for both the oxidation reaction and surface oxidation. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

3:00pm **SS-TuA-4 The Effects of Alkane Structure, Cluster Size, and Cluster Composition on Activity of Pt_n and Pt_nGe_m Catalysts for Cracking and Dehydrogenation***, **Autumn Fuchs**, Scott Anderson,* University of Utah*; Avital Isakov, Anastassia Alexandrova,* University of California at Berkeley

The high temperature dehydrogenation, cracking, and coking chemistry of n-butane and isobutane, catalyzed by sub-nanometer Pt_n/alumina and Pt_nGe_m/alumina catalysts will be presented.The mechanisms are explored by temperature programmed desorption (TPD) experiments with size-selected clusters deposited on alumina supports, and detailed DFT calculations.The calculations probe cluster geometric and electronic structures, including the effects of both Ge and carbon addition, and examine binding and activation of the C4 alkanes and alkenes.N-Butane is observed to dehydrogenate efficiently on Pt catalysts with and without Ge.For pure Pt_n, there is some coking initially, but the coking decays over time and the dehydrogenation activity increases slightly, i.e., coking is self-limiting and does not deactivate Pt_n for n-butane dehydrogenation.With Ge present, there is essentially no coking for n-butane, even in the initial reaction.In contrast, isobutane on pure Pt_n/alumina catalysts simply cokes with hydrogen evolved, with no significant alkene or diene products.Ge addition to the Pt_n does suppress coking for isobutane, resulting in C_4H_8 product formation, but only for the the Pt_7-based catalyst (Pt_7Ge_2/alumina).In addition, we find that both 2- and isobutene coke badly on Pt_n/alumina, deactivating the catalysts, and that coking is suppressed by Ge addition.This work was supported by the Air Force Office of Scientific Research (AFOSR FA9550-19-1-0261).

3:15pm **SS-TuA-5 Oxygen Passivation of Au Capped Niobium***, **Van Do**, Helena Lew-Kiedrowska, Sarah Willson,* University of Chicago*; Chi Wang,* National Cheng Kung University (NCKU), Taiwan*; Steven Sibener,* University of Chicago

Nb is the highest temperature elemental superconductor; however, its application in particle accelerators and quantum computers is limited by growth of native surface Nb oxides. Au capping layers have been shown to prevent deleterious Nb oxide growth but Au morphology, kinetics, and degree of passivation at various coverages on Nb have not been fully investigated. This work characterizes the physical deposition and oxygen contamination of sub-ML to 10 ML Au coverages on Nb(100). We analyze the physical features and chemical states of the surface using Scanning Tunneling Microscopy, X-ray and UV Photoelectron Spectroscopy, and Auger Electron Spectroscopy. Preliminary results show that a post-deposition anneal as low as 350 C causes Au island formation at Sub-ML to 1 ML coverages, substantially exposing Nb to oxidation. Thus, understanding the effects of temperature and coverage on Au formation will be critical for revealing the optimal method to passivate Nb.

4:00pm **SS-TuA-8 Achieving Effective Catalysis by Transient Heating Using Mechanocatalysis and Pulsed Joule Heating***, **David Sholl**, Zili Wu,* ORNL*; Carsten Sievers,* Georgia Institute of Technology*; Liangbing Hu,* Yale University **INVITED**

Transient heating can be a powerful approach to control the selectivity of catalytic reaction networks, especially for endothermic reactions where undesirable species can be formed under steady state conditions. Mechanocatalysis and pulsed Joule heating are two approaches where surface temperature changes of 500-1000 K can be achieved on millisecond timescales. This talk will discuss how a combination of experiments and computational simulations have been used to understand the reaction conditions that are accessible with these unconventional heating methods. Examples will include the use of computational modeling to probe temperature inhomogeneities in realistic models of carbon fiber supports during pulsed Joule heating and the use of single impact experiments and simulations to quantify heat delivery and chemical reactivity during mechanochemical depolymerization.

4:30pm **SS-TuA-10 Unraveling the Desorption Dynamics of Cyclic Hydrocarbons on Fe_3O_4(001): Insights from Temperature-Programmed Desorption***, **Moritz Eder**[1],* TU Wien, Austria*; Federico Loi,* J. Heyrovsky Institute of Physical Chemistry, Czechia*; Nail Barama, Faith Lewis, Margareta Wagner,* TU Wien, Austria*; Štefan Vajda,* J. Heyrovsky Institute of Physical Chemistry, Czechia*; Jiří Pavelec, Gareth Parkinson,* TU Wien, Austria

We investigate cyclic hydrocarbons — cyclohexane, cyclohexene, and benzene — on the magnetite Fe_3O_4(001) surface by means of temperature-programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS). Through a detailed analysis of the TPD profiles, we uncover distinct interaction mechanisms between these molecules and the Fe_3O_4(001) surface, shedding light on the role of molecular structure and surface chemistry. Despite the structural similarities, the adsorption energies and desorption orders and hence the interaction with the surface are different for each molecule. Furthermore, the desorption behavior differs from other surfaces previously investigated in the literature.[1,2] The results provide a deeper understanding of the substrate-surface interactions, with implications for catalytic applications, such as hydrocarbon upgrading, and the design of oxide-supported catalysts for energy and chemical industries.

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4:45pm **SS-TuA-11 Investigating the Stability and Reactivity of Subsurface Oxygen in Ag(111) Using Lattice-Gas Models, DFT, and Monte Carlo Simulations***, Carson Mize, Lonnie Crosby, Bright Daniel, **Sharani Roy,*** University of Tennessee Knoxville

First-row atoms, such as hydrogen, carbon, and oxygen, not only adsorb on the surface of a solid but are small enough to diffuse into the near-surface or subsurface region. The percolation of adsorbates through the surface

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[1] **JVST Highlighted Talk**

raises many fundamental questions, such as what conditions promote subsurface adsorption? Does the same adsorbate have different chemical properties in the subsurface compared to the surface? How do subsurface adsorbates influence chemical reactions on surfaces? To address these questions, we extended the theoretical framework of lattice-gas models to describe both coverage-dependent surface and subsurface adsorption in crystalline solids. Using this framework, we developed an all-site DFT-parameterized lattice-gas model for O/Ag(111) and integrated it with Monte Carlo simulations to calculate the thermodynamic distributions of atomic oxygen on the surface and in the subsurface of Ag(111). The results show that subsurface adsorption becomes thermodynamically favorable for oxygen coverages exceeding 0.375 ML. Furthermore, we applied the simulations to construct the first ab initio phase diagram of O/Ag(111) that shows the pressure and temperature ranges within which subsurface oxygen coexists with surface oxygen on Ag(111). Our results indicate that subsurface oxygen is present under the industrial conditions used for the catalytic partial oxidation of olefins on silver nanoparticles. Finally, we computed the reaction pathway for the conversion of ethylene to ethylene oxide on Ag(111) using DFT and found significant changes to the reaction barriers with increased oxygen coverage and the presence of subsurface oxygen.

5:00pm **SS-TuA-12 Size and Proximity Dependent Electronic Metal-Support Interactions on Cu/TiO$_2$(110)***, Lindsey Penland, H. H. Hirushan, N. Dissanayake,* ***Rachael Farber,*** University of Kansas

Electronic metal-support interactions (EMSI) are often cited as an origin of enhanced selectivity and efficiency of oxide-supported metal nanoparticle catalysts. While it is understood that tuning the oxide support defect density and metal nanoparticle size impacts the EMSI, it is unclear how such structural modifications attenuate the electronic landscape of the catalyst at the atomic scale. In this work, rutile TiO$_2$(110) was used as a strong Lewis acid oxide support to determine the spatially resolved electronic consequences of Cu nano-particle size on EMSI. Using a combination of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), the TiO$_2$(110) (1×1), (1×2), (1×3), and (2×2) surface reconstructions were characterized to reveal the relationship between the coordination number of Ti and the observed local density of states (LDOS). Following this characterization, sub-monolayer quantities of Cu were deposited on TiO$_2$(110) and annealed to either 100 °C, 300 °C, or 500 °C to promote Cu diffusion and aggregation. STS taken atop the Cu particles showed the emergence of electronic states within the bandgap of TiO$_2$(110). The intensity and position of these electronic states were strongly dependent on the size of the Cu particle. STS collected at the Cu/TiO$_2$(110) interface showed unique LDOS when compared to the LDOS of the Cu particle and the TiO$_2$(110), suggesting an attenuation of the electronic structure at the Cu/TiO$_2$(110) interface. This attenuation of the LDOS extended beyond the immediate Cu/TiO$_2$(110) interface, with the distance of attenuation related to the size of the Cu particle. These results highlight the real-space, heterogeneous electronic landscape of oxide-supported metal nanoparticle systems which may have significant implications for overall reactivity and selectivity.

5:15pm **SS-TuA-13 Steering Pt Cluster Dimensionality via Morphology and Surface Oxidation State of CeO2(111) Thin Films***,* ***Johanna Reich****, Mina Soltanmohammadi,* Technical University of Munich, Germany*; Vedran Vonk,* Deutsches Elektronen-Synchrotron (DESY), Germany*; Sebastian Kaiser, Ueli Heiz,* Technical University of Munich, Germany*; Andreas Stierle,* Deutsches Elektronen-Synchrotron (DESY), University of Hamburg, Germany*; Friedrich Esch, Barbara A. J. Lechner,* Technical University of Munich, Germany

Ceria has recently returned into the focus of research thanks to the possibility to reversibly form and redisperse supported, catalytically active Pt clusters by controlling its morphology and redox state. In the present work, we systematically synthesize CeO$_2$(111) thin films to tune these parameters independently and investigate their influence on size-selected Pt$_{20}$ cluster dimensionality and sintering behavior. First, we present recipes for atomically flat islands and closed CeO$_2$(111) films with a thickness up to 18 monolayers (ML), grown on Rh(111), and characterize them by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and low-energy electron diffraction (LEED). Remarkably, XRD and LEED show an epitaxially grown, crystalline, and relaxed film with cube-on-cube alignment. Bulk or exclusive surface reduction is achieved by ultra-high vacuum (UHV) annealing or room temperature (RT) CH$_3$OH dosing and annealing cycles, respectively. The methanol procedure forms oxygen vacancies only in the surface, without reducing the deeper layers of the film or introducing roughening. When deposited on a fully oxidized (Figure 1 (a,d)) versus a surface-reduced (Figure 1 (b,e)) support, Pt$_{20}$ clusters show a strikingly different temperature-dependent dimensionality and sintering behavior. From STM images, we extract detailed cluster height distributions and coverages (Figure 1 (c,f)) and find that Ostwald ripening already sets in around 600 K on both, oxidized and reduced supports, without any indication for cluster diffusion and coalescence. Notably, at these temperatures, we obtain flat 2D clusters on the reduced support and 3D clusters on the oxidized support, where the atom detachment during sintering leads to the intermediate formation of Pt^{2+} species, in line with the redispersed single atoms at step edges observed in the literature [1-3].

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Chemical Analysis and Imaging at Interfaces
Room 205 ABCD W - Session CA+AS+SS-WeM

Chemical Analysis and Imaging at Interfaces Oral Session

Moderators: Gabriel Parker, Oak Ridge National Laboratory, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SS-WeM-1 Heterogeneous Chemistry at Liquid-Vapor Interfaces Investigated by X-Ray Photoelectron Spectroscopy***, **Hendrik Bluhm**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Aqueous solution-vapor interfaces govern important phenomena in the environment and atmosphere, including the uptake and release of trace gases by aerosols and CO_2 sequestration by the oceans. A detailed understanding of these processes requires the investigation of liquid-vapor interfaces with chemical sensitivity and interface specificity. [1] This talk will discuss opportunities and challenges for investigations of liquid-vapor interfaces using X-ray photoelectron spectroscopy and describe recent experiments that have focused on the propensity of certain ions and the role of surfactants at the liquid-vapor interface.[2-4] The talk will also discuss the utilization of photoelectron angular distributions for the investigation of the depth of solvation of surfactants at the interface. [5-7]

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8:30am **CA+AS+SS-WeM-3 Probing Chemical and Catalytic Interfaces Using Operando Soft X-Ray Spectroscopy***, **Jinghua Guo**,* Lawrence Berkeley National Laboratory **INVITED**

Synchrotron based X-ray spectroscopic techniques offers unique characterization of energy, catalysis and chemical process in regards to the functionality, complexity of material architecture and chemistry. In the operando soft X-ray spectroscopy study of interfacial phenomena, it has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, such as the energy conversion and energy storage materials in the chemical and catalytic processes. This presentation will show how to best use the X-ray spectroscopy characterization techniques, including X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) to investigate the real interfacial reaction mechanism during the operation. The experimental results show how operando soft X-ray spectra uncover the phase conversion, chemical and structure change of solid/liquid and solid/gas interfaces in real time, thus further enhance the understanding of real reaction mechanism.

9:00am **CA+AS+SS-WeM-5 Capturing Electrical Double Layer in Action with Xps on a Graphene Coplanar Capacitor with an Ionic Liquid***, **Sefik Suzer**,* Bilkent University, Chemistry Department, Ankara, Turkey

Time-dependent XPS data is recorded for capturing the dynamics of the Electrical Double Layer formation on electrified two Multilayered-Graphene electrodes, configured as a coplanar-capacitor, having an ionic liquid as the electrolyte. The device is subjected to 2 V biasing cycle changing its polarity every hour, while iteratively recording the O1s peak representing the anion with 0.5 s steps. Variations in the O1s peak's binding energy position on the electrified electrode report directly the electrical potential of the IL medium, which suddenly jumps to the opposite polarization, if the electrode is grounded. The peak eventually returns to its equilibrium position with a relatively long time constant. The complementing action is also captured on the drain electrode, which exhibits mirrored but oppositely polarized temporal variations. Grounding the electrode allows separating the fast electronic components from those slow ionic ones, which is the key process introduced in this work, which is vital for better understanding of the function of the numerous components of the devices investigated. Experimental details will be given, these novel findings will be discussed and their implications for understanding the mechanism of the EDL formation will be presented.

9:15am **CA+AS+SS-WeM-6 Studying Tungsten and Alloys as Candidate Plasma Facing Material Using ToF-SIMS***, **Xiao-Ying Yu**, Gabriel Parker, Tobias Misicko, Yan-Ru Lin,* Oak Ridge National Laboratory*; Tanguy Terlier,* Rice University*; Yutai Katoh,* Oak Ridge National Laboratory

Plasma facing materials (PFMs) are important in realizing fusion power. Tungsten (W) and alloys are considered primary candidates of PFMs due to their high melting points, high thermal conductivities, good neutron irradiation resistance, fast diffusion of hydrogen, low retention, and sputtering behaviors. However, technical challenges remain in adopting W and alloys as PFMs. In this presentation, we will share recent study cases of W and alloys using advanced microanalysis and chemical imaging, primarily time-of-flight secondary ion mass spectrometry (ToF-SIMS). SIMS is a powerful imaging mass spectrometry tool, and it can be used to reveal surface composition with high sensitivity or probe the material layer-by-layer and reveal spatial distributions in two-dimension or three-dimension. Due to parallel data acquisition, full spectral information consisting of elements, isotopes, and molecule permitted in the duty cycle is available in SIMS' chemical mapping. We will present a few case studies of potential PFMs using SIMS. First, High Flux Isotope Reactor (HFIR) irradiated single crystal tungsten (SCW) specimens from the FRONTIER collaboration campaigns were selected for spectral analysis and depth profiling. SCW coupons were subjected to shielded and unshielded neutron irradiation in HFIR. Prior to ToF-SIMS analysis, specimens were prepared using focused ion beam (FIB). To assure reliable peak identification and assignment, we performed analysis of pristine single crystal tungsten as a control. Mass spectra reconstructed from depth profiling show a variety of transmutation products in unshielded W, such as Rhenium, Osmium, and Tantalum. In contrast, not as many transmutation products were detected in the shielded irradiated W spectra. Second, W alloys were studied to verify the trace doping quantity of Boron (B) using the high mass sensitivity of SIMS spectroscopy, and measurements were verified using Raman. Depth profiling was used to verify the distribution of B within the W matrix. Third, we show that depth profiling with high spatial resolution can be used to map the grain boundaries in W alloys and assist the development of new materials and validate the engineering process. These recent studies provide results of the structural and compositional changes in W and alloys as potential PFMs, showing that SIMS can be a useful tool on elucidating alloy property changes and supporting material development for sustainable fusion in the future.

11:00am **CA+AS+SS-WeM-13 ToF-SIMS Acquisition Multiplexing - Concept, Applications, and Data Analysis***, **Henrik Arlinghaus**,* 1) ION-TOF GmbH, Germany; 2) Institut für Hygiene, WWU, Germany*; Alexander Pirkl, Derk Rading, Julia Zakel, Ewald Niehuis,* ION-TOF GmbH, Germany **INVITED**

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a versatile technique for 2D and 3D analysis of surfaces. During the acquisition process, secondary ions are desorbed from the sample using one or more primary ion beams. These secondary ions are used to acquire a full mass spectrum at each voxel. Typically, a single acquisition mode is used when acquiring data, optimized for one specific potential aspect of the (unknown) sample. This becomes problematic when the number of acquisitions is constrained by the amount of sample available or the instrument time available. In the acquisition multiplexing approach, multiple acquisition modes, each of which is optimized for a specific performance aspect, are utilized during the acquisition process, resulting in multiple co-located datasets. Each of these acquired datasets may be analyzed individually in the traditional manner, or via algorithmic techniques such as Multivariate Statistical Analysis (MVSA) or Machine Learning (ML). Additionally, by taking advantage of the dataset's co-location property, it is possible to analyze all of the acquired data at once, finding aspects of the sample which span the data spectrally, spatially, and across acquisition modes.

We have applied this approach to vary numerous performance parameters of ToF-SIMS instruments, such as the primary ion beam current, the primary ion species, the focus of the beam, etc. Subsequently, analysis routines optimized for the parameter that was varied were applied to the datasets to make full use of the resulting data. One example is acquiring datasets using different primary ion beam currents, and then generating a High Dynamic Range (HDR) like dataset. High primary ion currents result in intense peaks which may saturate the detector signal. At the same time, low intensity signals are noisy at low primary ion currents. Another parameter which we varied is whether to optimize the primary beam for high mass resolution (and lower spatial resolution), or high spatial resolution (and lower mass resolution). This results in two datasets with fully complementary information. These may then be analyzed using machine learning based image fusion to generate a single high mass high spatial resolution dataset.

11:30am **CA+AS+SS-WeM-15 Diamond Surface Analysis for Electronics and Quantum Applications***, **Alastair Stacey**,* Princeton Plasma Physics Laboratory **INVITED**

Characterising and controlling surface electronic and quantum states is an almost ubiquitous challenge for electronic and quantum technologies. The diamond material system is a particular example, where bulk states can be created with extreme purity but surface states, chemical and physical, are not yet well controlled or even understood.

In this presentation I will detail our efforts to analyse the diamond surface, with a variety of vacuum science techniques and theoretical analyses, and reveal some of the chemical challenges being faced in passivating and functionalizing this surface. I will show evidence that these surfaces remain significantly disruptive for quantum devices and present recent efforts in the development of high performance hydrogen terminated diamond transistors. Finally, I will forecast the remaining challenges and next steps for improving the surface science of this important quantum electronic material.

12:00pm **CA+AS+SS-WeM-17 ToF-SIMS Spectral Analysis Using Python***, **Tobias Misicko**[1],* Louisiana Tech University and Oak Ridge National Laboratory*; Nan Jiang, Xinghang Zhang, Yexiang Xue,* Purdue University*; Xiao-Ying Yu,* Oak Ridge National Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful surface analysis technique that enables spatially resolved chemical characterization of materials with high mass resolution and accuracy. However, analyzing ToF-SIMS data remains challenging due to the high dimensionality and large size of datasets resulting from parallel data acquisition. Previous efforts have largely depended on manual interpretation and the analyst's prior experience to apply dimensionality reduction techniques for material composition analysis. This process demands substantial human supervision and is hindered by the lack of open-source datasets and comprehensive, end-to-end code implementations for multivariate analysis pipelines, particularly for principal component analysis (PCA) and non-negative matrix factorization (NMF). In this work, we integrate both established and emerging methods tailored for ToF-SIMS spectral analysis, delivering an open-source, Python-based framework for intelligent mass spectral analysis to the ToF-SIMS research community. We demonstrate the application of PCA and NMF for spectral analysis and benchmark their performance using a quality-assured SIMS dataset.

Surface Science
Room 209 CDE W - Session SS-WeM
On Surface Reactions

Moderators: Nathan Guisinger, Argonne National Laboratory, USA, **Yuan Zhang**, Old Dominion University

8:00am **SS-WeM-1 Surface and Interface Induced Properties of Low-dimensional Materials: First Principle Simulations***, **Shixuan Du**,* Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Two-dimensional (2D) materials, with their atomic-scale thickness and dangling bonds free surfaces, provide a unique platform for precisely modulating material properties via surface or heterointerface engineering. These approaches not only enhance existing properties but also induces novel emergent phenomena. In this report, I will talk about the chemical reactions happened on surfaces and the corresponding activation enhanced by the adsorption of the precursor molecules at specific site. Second, the coupling of multiple order parameters in 2D monolayers and bilayers will be discussed. The coupling allows for the manipulation of properties such as spin polarization, electronic band topology, and valley polarization. Finally, I will talk about the construction of electride-metal heterostructure and its application in ammonia synthesis.

References:

[1] Gao, Y.; Huang, L. et al. Nature Commun. 2022, 13, 6146.

[2] Yang, J.; Pan J. et al. J. Am. Chem. Soc. 2024, 146, 21160−21167.

[3] Zhang Y.-F.; Guo H. et al. Adv. Funct. Mater. 2024, 34, 2410240.

[4] Pan, J.; Zhang Y.-F. et al. Nano Lett. 2024, 24, 14909–14923.

8:30am **SS-WeM-3 In situ XPS Study of Pt-Grafted g-C3N4 as a Water-Splitting Photocatalyst***, Yu-Bin Huang,* National Synchrotron Radiation Research Center, Taiwan*; Ying-Huang Lai,* Department of Chemistry, Tunghai University, Taiwan*; **Bo-Hong Liu**[2],* National Synchrotron Radiation Research Center, Taiwan

The generation of hydrogen through solar-light-driven water splitting has acquired significant research interest, owing to the abundant availability of water as a raw material and the virtually limitless energy provided by sunlight. Graphitic carbon nitride (g-C_3N_4) has emerged as a promising catalyst due to its cost-effectiveness and eco-friendly characteristics.[1] When metal atoms are grafted onto g-C_3N_4, the chemical properties of the resulting metal/g-C_3N_4 composite can be optimized to enhance catalytic performance. Among various analogs, the single-atom Pt / g-C_3N_4 composite demonstrates exceptional catalytic reactivity.[2] This enhanced performance can be attributed to the metal-to-ligand charge transfer, which shifts the absorption spectrum toward the solar energy maximum. Additionally, the isolated Pt atom serves as a redox active site, significantly improving reaction kinetics.

In this presentation, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) investigation of Pt-grafted g-C_3N_4 under the conditions of photocatalytic water splitting. The binding energy shifts observed upon exposure to solar light provide insights into the charge transfer dynamics between the Pt and the g-C_3N_4. Furthermore, the presence of water vapor during illumination induces changes in Pt, C, and N spectra, suggesting the existence of surface adsorbates and/or surface reaction intermediates. The work function shift of the catalyst is monitored through gas phase peaks under the reaction condition. These findings deepen our fundamental understanding of the mechanisms underlying g-C_3N_4-based water-splitting catalysts at the atomic level, providing valuable guidance for the development of g-C_3N_4-based photocatalytic systems.

References:

1. Zheng, Y.; Lin, L.; Wang, B.; Wang, X., Graphitic carbon nitride polymers toward sustainable photoredox catalysis. *Angewandte Chemie International Edition* **2015,** *54* (44), 12868-12884.

2. Kuang, P.; Wang, Y.; Zhu, B.; Xia, F.; Tung, C. W.; Wu, J.; Chen, H. M.; Yu, J., Pt single atoms supported on N-doped mesoporous hollow carbon spheres with enhanced electrocatalytic H2-evolution activity. *Advanced Materials* **2021,** *33* (18), 2008599.

8:45am **SS-WeM-4 Hydrogen-Induced Surface Chemistry of Copper Boride on Cu(111)***, **Jennifer Sanchez**, Kevin Sutherland,* University of Texas at San Antonio*; Abdullah Al-Mahboob,* Brookhaven National Laboratory*; Fang Xu,* University of Texas at San Antonio*; Dario Stacchiola,* Brookhaven National Laboratory

A new type of 2D boron-based materials has potential applications in a variety of fields including energy, devices, and catalysis. However, the material needs to be physically stabilized by a single crystal substrate and is chemically unstable. When Cu(111) is used as the substrate, there is a debate on whether borophene or copper boride is formed. In this work, we present results to identify the chemical identity of the boron-formed layer on Cu(111) and further study the reduction by atomic hydrogen as a strategy to stabilize the formed 2D boron materials. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) resolve the surface structure. *In-situ* X-ray photoelectron spectroscopy (XPS) identifies Cu-B bonding, and low-energy electron microscopy intensity-voltage (LEEM-IV) measurements reveal the work-function shift, indicating strong evidence of copper boride formation. We find that the copper boride surface readily reacts with atomic hydrogen, suggesting new opportunities to influence surface chemistry and explore catalytic functionality.

9:00am **SS-WeM-5 DFT Study of Transition-Metal Doping in $Ni(OH)_2$/NiOOH Catalysts for Enhanced Urea Oxidation***, Qiu Jin, Matteo Garcia-Ortiz,* School of Chemical, Biological, and Environmental Engineering, Oregon State University*; **Líney Árnadóttir**[3],* School of Chemical, Biological, and Environmental Engineering, Oregon State University. Physical and Computational Sciences Directorate, Institute for Integrated Catalysis, Pacific Northwest National Laboratory

Urea is commonly found in agricultural runoff and wastewater, where it can disrupt nutrient cycles and harm aquatic ecosystems. Urea is also a promising sustainable energy source for fuel cells and hydrogen generation through electrochemical urea oxidation (UOR). Identifying suitable catalyst

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

[3] **JVST Highlighted Talk**

material for UOR is challenging due to a complex six-electron transfer mechanism, with high overpotential, and competition with the oxygen evolution reaction (OER). Here we use density functional theory (DFT) calculations to investigate how five metal dopants (Mn, Fe, Co, Cu, Zn) influence UOR activity on basal-plane sites of β-NiOOH, the phase transition from β-Ni(OH)$_2$ to catalytically active β-NiOOH, and the UOR-OER selectivity.

We show that doping β-Ni(OH)$_2$ accelerates surface dehydrogenation, facilitating its transformation into the active β-NiOOH phase. Mn and Fe doping also enhances dehydrogenation and reduces the Gibbs free energy of UOR, promoting reaction efficiency. On the other hand, Cu doping reduces UOR activity and has little effect on the phase transition. Additionally, Mn increases the OER limiting potential, benefiting the competition between UOR and OER while Cu lowers the OER overpotential, reducing the potential window of higher UOR activity. These insights elucidate the interplay between dopants, phase stability, and reaction selectivity, advancing the design of high-performance catalysts for urea-rich wastewater treatment and energy conversion technologies.

9:15am **SS-WeM-6 Visualizing Self-Metalation Mediated Cyclodehydrogenation of a Nonplanar Tetrabenzoporphyrin Molecule by Tip-Enhanced Raman Spectroscopy***, **Soumyajit Rajak**[1], Nan Jiang,* University of Illinois, Chicago

Opto-electronic properties of functional molecular materials are controlled by local nanostructures constructed by the molecular arrangements at the nanoscale and their local chemical environment. Metal surface-supported physicochemical transformations facilitate the tuning of structural and electronic properties of functional materials. To obtain a higher degree of control over the reaction outcome, submolecular scale characterization of the chemical intermediates and their local environment is required. Determining the real-space surface adsorbed configurations of molecules is challenging using ensemble-averaged surface science techniques. Again, probing the effect of the local environment of chemical species is challenging because the spatial resolution of conventional optical spectroscopic techniques is limited by the diffraction limit of light. Coupling light with plasmonic nano-objects creates highly localized surface plasmons (LSPs), which allows us to break the diffraction limit. Herein we explore tetraphenyl-tetrabenzoporphyrin molecules as one of the most widely studied model molecules in organic optoelectronics for modern-age electronic device applications and catalysis. We present a combined topographical and chemical analysis of different surface-adsorbed configurations and surface-sensitive arrangements of a tetrabenzoporphyrin molecule and their chemical reactivity on a metal surface using angstrom-scale resolution scanning tunneling microscopy (STM) and ultra-high vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Low temperature (77K) scanning tunneling microscopic images and localized surface plasmon resonance enhanced Raman signals reveal different adsorbate configurations of molecular entities and their thermal reaction products with a fundamental view of adsorbate-substrate binding interactions. The atomic scale insights obtained into the local environment enable precise control over the fabrication of molecules with tailored optoelectronic properties.

9:30am **SS-WeM-7 Band Engineering Low Energy States in 1D and 2D Carbon Nanomaterials***, **Felix Fischer**,* UC Berkeley **INVITED**

Our research focuses on the rational design, deterministic assembly, and detailed investigation of the physical phenomena emerging from quantum confinement effects in carbon nanomaterials. We pursue a highly integrated multidisciplinary program, founded on synthetic bottom-up approaches toward functional materials with precisely defined structure. We control their assembly into hierarchically ordered architectures and evaluate inherent physical properties using modern scanning probe techniques cross multiple length, time, and energy scales.

Here we describe two new classes of low-dimensional carbon nanomaterials: The first represents a dual-square carbon-oxide lattice featuring a Dirac nodal-line semimetal (DNLSM) band structure. Orbital engineering guided by Wannier function analysis guided the design of a *d4mm* symmetrictetraoxa[8]circulene (TOC) covalent-organic framework linked through cyclobutadiene groups. A second example describes the realization of phase frustration induced flat bands in a diatomic Kagome lattice. The chemical stabilization of the energetically unfavorable open-shell high-spin ground state of aza-[3]triagnulene within the lattice of a COF forms the basis for a degenerate set of molecular orbitals that give rise to hopping frustrated topological flat bands near the Fermi level.

References

[1]Liu, F.; Yan, Y.; Tang, W.; Qie, B.; Chen, J.; Wang, Z.; Louie, S. G.; Fischer F. R. Orbital Engineering Band Degeneracy in a Dual-Square Carbon-Oxide Framework, **2025**, *under review*.

[2]Yan, Y.; Liu, F.; Tang, W.; Qie, B.; Louie, S. G.; Fischer F. R. *Engineering Phase-Frustration Induced Flat Bands in an Aza-Triangulene Covalent Organic Kagome Lattice*, **2025**, *under review*.

11:00am **SS-WeM-13 On-Surface Synthesis and Single-Molecule Manipulation for the Atomically Precise Fabrication of Carbon Nanomaterials***, **J. Michael Gottfried**,* University of Marburg, Germany **INVITED**

Recent advancements of on-surface synthesis techniques enable the fabrication and precise characterization of carbon-based nanomaterials with atomic-scale accuracy. These materials often exhibit novel (opto-)electronic and magnetic properties, which are partly derived from the inherent characteristics of the precursor molecules and partly emerge from the unique structures formed during synthesis. Therefore, on-surface synthesis presents a highly versatile alternative to conventional solution-phase chemistry, leading to novel products not obtainable by conventional chemical methods. Specifically, the quest for nonbenzenoid sp^2 carbon allotropes has stimulated substantial research efforts because of their predicted unique mechanical, (opto-)electronic, and transport properties. However, synthesis of these carbon networks remains challenging due to the lack of reliable protocols for generating nonhexagonal rings. We have developed various on-surface synthesis strategies by which polymer chains are linked to form nonbenzenoid carbon networks. In this way, we synthesized biphenylene network, a carbon allotrope with 4-6-8-membered rings, which is metallic already at very small dimensions, and other carbon networks. [1]

An especially rigorous protocol for the prototyping of new materials is the direct manipulation of atoms and molecules with the tip of a low-temperature scanning tunneling microscope. Here, we used this method to fabricated tridecacene (13ac) and pentadecacene (15ac), the longest acenes achieved to date, via multistep single-molecule manipulation. [2,3] Acenes are another important class of carbon materials with potential for use in organic electronics. We find antiferromagnetic open-shell ground state electron configurations for both acenes. Notably, 15ac shows a low-bias spin-excitation feature, indicating a singlet-triplet gap of around 124 meV. Investigation of 15ac complexes with up to 6 gold atoms suggest considerable multiradical contributions to the electronic ground state of 15ac. [3] Furthermore, doping with heteroatoms alters the electronic and magnetic properties of carbon-based nanomaterials. We present a variety of nitrogen-containing carbon nanostructures including planar and curved cycloarenes as well as N-doped graphene nanoribbons.

[1] Q.T. Fan, L-H. Yan et al., J.M. Gottfried, Science 372, 852-856 (2021).

[2] Z.L. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. 146, 3700-3709 (2024).

[3] Z.L. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. 147, 4862–4870 (2025).

11:30am **SS-WeM-15 Impact of Subsurface Oxygen on CO Oxidation over Rhodium Surfaces***, Arved Dorst,* University of Göttingen, Germany*; Maxwell Gillum, Daniel Killelea,* Loyola University Chicago*; **Tim Schäfer**,* University of Göttingen, Germany

Rhodium surfaces play a crucial role in heterogeneous catalysis, driving extensive research on their reactivity. In particular, CO oxidation is of great interest, where different oxygen species at the surface can influence catalytic activity. Under certain conditions, rhodium can also host subsurface oxygen species, further affecting reaction dynamics. In this work, we combine molecular beam surface scattering, ion imaging, and ultra-high vacuum techniques to investigate the impact of subsurface oxygen on CO oxidation on single-crystal Rh surfaces. When oxidizing CO at the (2 × 1)-O adlayer without subsurface oxygen, we observe hyperthermal velocity distributions of desorbing CO_2, indicating significant energy release along the translational coordinate directly from the transition state. In contrast, the presence of subsurface oxygen results in thermal velocity distributions, suggesting the formation of a temporarily trapped chemisorption state, which becomes energetically favorable in the presence of subsurface oxygen.

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

11:45am **SS-WeM-16 Structural Elucidation of Intermediates in the Selective Epoxidation Reaction of Ethylene on Ag(111) and NiAg(111)**, ***Dennis Meier***, *Elizabeth E. Happel,* Tufts University; *Matthew M. Montemore,* Tulane University; *E. Charles H. Sykes,* Tufts University

Ethylene epoxidation with molecular oxygen (O_2) to form ethylene oxide (EO) is a major industrial process. EO plays a significant role as a chemical intermediate for products such as pharmaceuticals, detergents, plastics, or antifreeze. Silver-based nanoparticles on alumina, enhanced with promoters like chlorine, rhenium, and cesium, are the primary catalysts for ethylene epoxidation. The key parameter for industrial ethylene epoxidation catalysts is their selectivity, as this reaction alone accounts for 3% of the CO_2 emissions from the chemical industry. There are two main surface oxygen species reported on silver: nucleophilic and electrophilic oxygen. The electrophilic species is thought to be selective for epoxidation, whereas nucleophilic oxygen is reported to be active for total combustion reaction of ethylene and EO to CO_2. Despite the significance of this reaction, the mechanism is still under debate. Recently, Ni was discovered to be a new promoter of the ethylene epoxidation adding 25% selectivity over pure Ag, an effect as large as Cl, the ubiquitous promoter.

Therefore, there is a great opportunity to understand the effect of Ni and the catalytic mechanism by which it operates to further improve process efficiency. We have performed an atomic-scale investigation of how Ni promotes oxygen activation and spillover on Ag as well as the surface intermediates of the reaction. Using a surface science approach in ultra-high vacuum (UHV) we investigated Ag(111) and NiAg(111) surfaces as a function of oxygen and ethylene exposure, Ni loading and the effect of temperature. An advantage of the NiAg system is that reactive species like NO_2 or ozone are not required to form atomic oxygen on silver in UHV meaning the system can be prepared without impurities. Using low-temperature scanning tunneling microscopy we directly image carbonate structures that are reported to be present in significant amounts on working epoxidation catalysts and may affect selectivity. We also report a precursor to surface carbonate formed from CO and electrophilic oxygen. The electronic structure of these species is probed with scanning tunneling spectroscopy and reactivity with temperature-programmed desorption measurements. Density functional theory is used to model the structure and formation of these carbonate structures and their precursors. Together, these data provide detailed insights into the structure and energetics of several chemical intermediates in the ethylene epoxidation reaction, which is crucial information for modeling and understanding the mechanism.

12:00pm **SS-WeM-17 Beyond Optimization: Exploring Novelty Discovery in Autonomous Experiment**, ***Ralph Bulanadi***, *Jawad Chowdhury,* Oak Ridge National Laboratory; *Hiroshi Funakubo,* Institute of Science Tokyo, Japan; *Maxim Ziatdinov,* Pacific Northwest National Laboratory; *Rama Vasudevan,* Oak Ridge National Laboratory; *Arpan Biswas,* University of Tennessee, Knoxville; *Yongtao Liu,* Oak Ridge National Laboratory

Autonomous experiments (AEs) are transforming how scientific research is conducted by integrating artificial intelligence with automated experimental platforms. Current AEs primarily focus on the optimization of a predefined target; while accelerating this goal, such an approach limits the discovery of unexpected or unknown physical phenomena. Here, we introduce a novel framework, INS2ANE (Integrated Novelty Score–Strategic Autonomous Non-Smooth Exploration), to enhance the discovery of novel phenomena in autonomous experimentation. Our method integrates two key components: (1) a novelty scoring system that evaluates the uniqueness of experimental results, and (2) a strategic sampling mechanism that promotes exploration of under-sampled regions even if they appear less promising by conventional criteria. We validate this approach on a pre-acquired dataset with a known ground truth comprising of image–spectral pairs. We further implement the process on autonomous scanning probe microscopy experiments. INS2ANE significantly increases the diversity of explored phenomena in comparison to conventional optimization routines, enhancing the likelihood of discovering previously unobserved phenomena. These results demonstrate the potential for AE to enhance the depth of scientific discovery; in combination with the efficiency provided by AEs, this approach promises to accelerate scientific research by simultaneously navigating complex experimental spaces to uncover new phenomena.

2D Materials
Room 208 W - Session 2D+EM+NS+QS+SS+TF-WeA

2D Materials: Synthesis and Processing

Moderator: Tiancong Zhu, Purdue University

2:15pm **2D+EM+NS+QS+SS+TF-WeA-1 Process Discovery for Quantum Materials***, **Stephan Hofmann**,* University of Cambridge, UK **INVITED**

Effective heterogeneous integration of low-dimensional nanomaterials in applications ranging from quantum electronics to biomedical devices requires a detailed understanding of different formation and interfacing reactions and the ability to synergize these processes. Process development largely still follows an Edisonian trial-and-error approach, blind and constraint by conventional reactors. This is not only wasteful and frustratingly slow, but hinders scientific breakthroughs in crystal growth and innovation in new deposition technology. This talk will focus on our cross-correlative, high-throughput operando approaches and combinatorial close-space sublimation (CSS) based process design to accelerate process discovery. We show operando spectroscopic imaging ellipsometry and scanning electron microscopy with machine-learning assisted analysis and parameter space exploration for salt-assisted WS_2 layer CVD and TMD oxidation phenomena, and howdirect kinetic process data can open data driven approaches to advance the required understanding of underpinning mechanisms.[1] We show that CSS is a highly promising alternative to conventional powder-furnace chemical vapour deposition, offering superior efficiency, precise structural control, scalability, and adaptable process designs. As part of processability and stability assessment, we also explore oxidation kinetics of TMD materials, [2] aided by atomistic modelling using machine-learned force fields.[3]

[1] Yang et al., Chem. Mat. 37, 989 (2025)

[2] Sahota et al., ACS Appl. Nano Mat., asap (2025)

[3] Gsanyi et al., arXiv:2401.00096, 2023

2:45pm **2D+EM+NS+QS+SS+TF-WeA-3 Selective Area Epitaxy of van der Waals Materials***, **Ryan Trice**[1], Stephanie Law,* Penn State University

Two-dimensional (2D) van der Waals (vdW) materials are interesting for a variety of applications, ranging from optoelectronics and photocatalysis to energy storage and topological devices. However, vdW materials synthesized using common techniques like chemical or physical vapor deposition often have a high density of growth-related defects, including grain boundaries, twin defects, pyramidal growth, and spiral defects. While pyramidal growth can be minimized through higher growth temperatures, grain boundaries, twin defects, and spiral defects are much harder to overcome. For many applications, especially in electronics and optics, these defects lead to non-radiative recombination, electron scattering, and other undesirable effects. Furthermore, the fabrication of 2D materials into quantum dots (QDs) through bottom-up methods faces problems with precise location placement and polydispersity in the QDs' diameters. This makes the QDs difficult to characterize and is not ideal for most quantum computing and optical setups. Top-down nanofabrication approaches fix this issue but often cause significant damage to the surfaces or edges of the materials. To address these issues, we used molecular beam epitaxy (MBE) combined with selective area epitaxy (SAE) to grow Bi_2Se_3 thin films. SAE is a technique in which thin films nucleate and grow in defined areas on a wafer. This is done using a patterned mask where growth conditions are selected such that the film will only nucleate on the substrate.

In this talk, we will describe SAE growth of Bi_2Se_3 on Al2O3 (0001) and Si (111) substrates using an atomic layer deposition SiO2 mask. Etching of the SiO2 mask was done with a wet chemical etch, resulting in micron-scale holes of various shapes and sizes. The processed substrates were then loaded into an MBE chamber for the growth of the Bi_2Se_3 film. First, we will discuss the effects of different substrate temperatures on the selective growth of the Bi_2Se_3 thin films. Second, we will discuss the geometric influence of variously shaped patterns on the crystal quality of the selectively grown films. Third, we will look at the effect and viability of nano-scale patterns for selective growth of vdW materials. Further studies will focus on using different materials for the substrate and mask. This approach could allow us to grow wafer-scale, defect-free 2D vdW QDs at specified areas on the wafer, thereby increasing the scalability and applicability of these materials to real-world challenges.

3:00pm **2D+EM+NS+QS+SS+TF-WeA-4 Precision Synthesis and Conversion of 2D Materials by Pulsed Laser Deposition with in Situ Diagnostics***, **Daniel T. Yimam**[2], Sumner B. Harris,* Oak Ridge National Laboratory, USA*; Austin Houston,* University of Tennessee Knoxville*; Ivan Vlassiouk,* Oak Ridge National Laboratory, USA*; Alexander Puretzky,* Oak Ridge National Laboratory*; Gerd Duscher,* University of Tennessee Knoxville*; Kai Xiao,* Oak Ridge National Laboratory, USA*; David B. Geohegan,* University of Tennessee Knoxville

Over the past few decades, 2D monolayers and heterostructures have become central to nanoscience, offering promising applications in electronics, sensing, and future computing. In addition to their exciting functional properties, significant progress has been made in their bottom-up synthesis and subsequent processing. Techniques such as encapsulation, doping, and implantation in atomically thin 2D materials are crucial to transitioning them from fundamental research to scalable, real-world applications, while enabling the emergence of novel properties. However, the ultrathin nature that makes 2D materials attractive also poses substantial challenges for traditional plasma-based processing methods. To fully harness the potential, it is essential to develop reliable processing techniques that offer precise control and reproducibility.

Pulsed laser deposition (PLD) is a promising non-equilibrium method that allows precise control over the kinetic energy (KE) of ablated species. In this work, we investigate plasma plume interactions with 2D materials using *in situ* plasma diagnostics and optical characterization tools. We demonstrate that a deep understanding and control of plasma plume dynamics enables new approaches for 2D material engineering, including the formation of Janus monolayers, metal atom implantation, and encapsulation with minimal damage. Our approach allows for low temperature substitution and implantation of foreign atoms, such as chalcogens and metals, facilitating the selective synthesis of Janus monolayers and alloys. These findings highlight the potential of PLD to drive the practical advancements in 2D materials for microelectronics and quantum information science.

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Keywords: Pulsed laser deposition, chalcogenide substitution, 2D materials, implantation, in situ diagnostics.

3:15pm **2D+EM+NS+QS+SS+TF-WeA-5 AVS Peter Mark Memorial Award Talk: Exploiting Thin Film Phase Diagrams for Synthesizing 2D Transition Metal Dichalcogenides***, **Nicholas R. Glavin**,* Air Force Research Laboratory **INVITED**

Synthesis of 2D transition metal dichalcogenides for specific applications in electronics, optoelectronic, and advanced coatings remains a critical bottleneck for many industrial applications. In this talk, we will highlight leveraging thin film phase diagrams to rapidly explore the vast parameter space in synthesizing these novel materials. This technique uses laser processing to locally modify regions within the film and coupled with high throughput characterization, rapidly assesses material state and quality for next generation sensors, optical coatings, and low power electronics.

4:15pm **2D+EM+NS+QS+SS+TF-WeA-9 Designer van der Waals Materials for Quantum Optical Emission***, Shengxi Huang, **Wenjing Wu**,* Rice University **INVITED**

Designer van der Waals (vdW) materials offers enormous opportunities to tune material properties for various applications. Isolated, optically-active defects generated in vdW materials could lead to single photon emission. 2D vdW materials as host materials for single photon emission hold various advantages, such as high optical extraction efficiency from the atomically-thin layered materials, and readiness to integrate with on-chip photonic and electronic devices. However, single photon emission from 2D vdW materials typically suffers from low purity and lack of controllability, due to the sensitivity of these atomically-thin materials to external dielectric environments, surface defects and adsorbents, and strains and wrinkles introduced during material processing. This talk introduces our recent efforts to improve the single photon purity and controllability in vdW materials. We developed novel defect structures that can overcome several current issues, and explored their electronic structure and tunability in optical emission. Through a combination of approaches, including strain engineering, heterostacking, employing optical selection rules for excitation and detection, optimization of material synthesis and handling, we were able to achieve high purity (> 98%) for single photons emitted from 2D

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

transition metal dichalcogenides (TMDs) at cryogenic temperature and in hBN at room temperature. This work provides deep insights into the electronic, spin, and valley properties of TMDs and hBN. It also paves the way towards the application of 2D vdW materials for quantum optical applications. The materials engineering approaches developed here can be applied to the optimization of other optical and quantum materials.

4:45pm **2D+EM+NS+QS+SS+TF-WeA-11 Macroscopic Tin Monochalcogenide Van Der Waals Ferroics: Growth, Domain Structures, Curie Temperatures and Lateral Heterostructures***, **Eli Sutter**, Peter Sutter,* University of Nebraska - Lincoln

2D and layered van der Waals crystals present opportunities for creating new families of ferroics with switchable electric polarization, elastic strain, or magnetic order at thicknesses down to the single-layer limit. Synthesis, however, typically leads to small crystals with sizes ranging from below 100 nm (e.g., for SnTe ferroelectrics) to a few µm (e.g., for SnSe ferroelectrics). The limited size and proximity to edges affects the ferroelectric and ferroelastic domain patterns, restricts the experimental methods available to probe emerging properties, and severely limits the ability to fabricate complex device architectures required for accessing functionalities in van der Waals ferroelectrics.

Here, we report the realization of in-plane ferroelectric few-layer crystals of the monochalcogenides tin(II) sulfide and selenide (SnS, SnSe) whose linear dimensions exceed the current state of the art by up to one order of magnitude. Such large crystals allow the investigation of ferroic domain patterns that are unaffected by edges and finite size effects. Analysis of the abundant stripe domains by electron microscopy and nanobeam electron diffraction shows two distinct domain types, twin domains separated by positively charged walls with alternating head-to-head and tail-to-tail polarization as well as not previously observed purely rotational domains connected by neutral domain walls with head-to-tail dipoles. Access to large ultrathin crystals allowed determining the Curie temperatures of few-layer SnSe[1] and SnS van der Waals ferroelectrics.

Finally, we demonstrate the integration of the ultrathin ferroelectric SnSe and SnS into lateral heterostructures.[2] A two-step process produces crystals comprising an SnSe core laterally joined to an SnS edge-band, as confirmed by Raman spectroscopy, electron microscopy imaging, and diffraction. The ability of the lateral interface to direct excited carriers, probed by cathodoluminescence, shows electron transfer over 560 nm diffusion length from the SnS edge-band. The ferroelectric heterostructures adopt two domain configurations, with domains either constrained to the SnSe core or propagating across the entire SnSe-SnS flakes.

The combined results demonstrate industrial scale in-plane ferroelectrics as well as multifunctional van der Waals heterostructures, presenting extraordinary opportunities for manipulating ferroelectric domain patterns and carrier flow**.**

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5:00pm **2D+EM+NS+QS+SS+TF-WeA-12 Machine Learning Analysis of Molecular Beam Epitaxy Growth Conditions***, Mingyu Yu, Ryan Trice, Isaiah Moses, Wesley Reinhart, **Stephanie Law**,* Penn State University

Machine learning models hold the potential to explore parameter space autonomously, quickly establish process-performance relationships, and diagnose material synthesis in real time. This reduces reliance on manual intervention in parameter space exploration, enabling more precise and efficient mechanistic control. For molecular beam epitaxy (MBE), despite its breakthroughs in materials synthesis, its stringent growth conditions and complex epitaxial mechanisms make the process of optimizing growth process time-consuming and expensive. Therefore, leveraging machine learning to develop autonomous MBE growth platforms presents a highly promising prospect.Our study on the multi-modal machine learning-guided MBE synthesis is based on a comprehensive high-quality dataset of GaSe thin films grown on GaAs (111)B substrates.GaSe is an emerging two-dimensional semiconductor material with intriguing properties, including thickness-tunable bandgaps, nonlinear optical behaviors, and intrinsic p-type conductivity.Moreover, as a representative member of the van der Waals (vdW) chalcogenide semiconductor family,insights gained from studying GaSe can be extended to other vdW chalcogenides. In this work, we aim to leverage machine learning to analyze the relationships between growth conditions (Ga flux, Se:Ga flux ratio, and substrate temperature) and the resulting sample quality, as well as the correlations among various characterization results including in situ RHEED patterns and ex situ x-ray diffraction rocking curve full-width at half maximum (FWHM) and atomic force microscopy (AFM) root mean square (RMS) roughness. Unsupervised learning on RHEED patterns reveals a well-defined boundary between high- and low-quality samples, capturing physically meaningful features. Mutual information analysis shows a strong correlation between RHEED embeddings and rocking curve FWHM, while the correlation with AFM RMS roughness is weak. Among key growth conditions, growth rate most strongly influences FWHM, whereas the Se:Ga flux ratio primarily affects RMS roughness and the RHEED embeddings. Supervised learning models trained to predict FWHM and RMS roughness demonstrate moderate accuracy, with significant improvement achieved by incorporating RHEED embeddings. Furthermore, anomaly detection via residual analysis in supervised learning aligns well with unsupervised classification from RHEED, reinforcing the reliability of the predictive models. This study establishes a data-driven framework for machine learning-assisted MBE, paving the way for real-time process control and accelerated optimization of thin-film synthesis.

5:15pm **2D+EM+NS+QS+SS+TF-WeA-13 Promoting Crystallographic Alignment in SnSe Thin Films using Step Edges on MgO by MBE***, **Jonathan Chin**, Marshall Frye, Joshua Wahl, Kayla Chuong,* Georgia Institute of Technology*; Mengyi Wang, Derrick Liu,* Pennsylvania State University*; Mingyu Yu,* University of Delaware*; Qihua Zhang, Nadire Nayir, Adri van Duin, Maria Hilse, Stephanie Law,* Pennsylvania State University*; Lauren Garten,* Georgia Institute of Technology

SnSe is a van der Waals material that can be scaled down to two dimensions,[1] making it a promising candidate for nanoelectronics such as field effect transistors (FETs).[2] SnSe in the orthorhombic *Pnma* structure exhibits significant electrical anisotropy where thecarrier mobility is 45% higher along the [010] direction than the [001] direction in plane,[3] making it necessary to control the in-plane alignment of 2D films for integration into electronic devices. SnSe has been shown to form planar coverage on (100) MgO,[4] with which it has a 1.4% and 5.5% lattice mismatch along the [010] and [001] directions, respectively. However, despite the distinct axial lattice matches, in-situ reflective high-energy electron diffraction (RHEED) shows no preferential SnSe film alignment for films deposited on uncleaved MgO. Therefore, to promote orientation control, we cleaved and annealed the MgO substrates to produce step edges along the surface to increase the local surface energy, thereby encouraging atomic adsorption and alignment. SnSe thin films were then deposited from individual Sn and Se effusion cells via molecular beam epitaxy (MBE) onto the prepared MgO substrates heated to 280 °C for 1-5 minutes with a 1.35:1.00 Se:Sn flux ratio at a 0.083 Å/s growth rate to track the nucleation and growth of SnSe grains. The phase of the SnSe films was confirmed by Raman spectroscopy, exhibiting the characteristic A_g^2, B_{3g}, A_g^3, and A_g^4 phonon modes.[5] In-situ RHEED confirmed the in-plane alignment along the [010] and [001] by RHEED relative to the [100] substrate, matching theory projections made using reactive force field (ReaxFF) simulations. Additionally, atomic force microscopy (AFM) shows SnSe grains nucleating at step edges on MgO, while scanning transmission electron microscopy (STEM) reveals how the aligned SnSe grains propagate laterally off step edges, maintaining crystallographic alignment throughout the film layer. Overall, our results demonstrate that SnSe grains preferentially nucleate along the step edges produced parallel to the [100] edge of the MgO substrates. The alignment of a 2D vdW film facilitated by step edge formation demonstrates how to achieve orientated depositions of similar anisotropic vdW films on a substrate of choice, ultimately facilitating the manufacture of 2D nanoscale electronic devices.

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5:30pm **2D+EM+NS+QS+SS+TF-WeA-14 Synthesis of Millimeter-Scale Single-Crystal α-MoO_3 Nanosheets on Sapphire***, **Ryan Spangler**,* Pennsylvania State University*; Thiago Arnaud, Joshua Caldwell,* Vanderbilt University*; Jon-Paul Maria,* Pennsylvania State University

α-MoO_3 is a van der Waals layered semiconductor with biaxial anisotropy that has recently gained interest as an emerging 2D material with a wide band gap (~3 eV), large work function, and high permittivity. Additionally, α-

MoO_3 exhibits extreme anisotropy of the dielectric function, enabling in-plane and out-of-plane elliptic or even hyperbolic behavior at various wavelengths. Therefore, α-MoO_3 also possesses great potential for nanophotonics through the low-loss and directional propagation of hyperbolic phonon polaritons, which result from the interaction of light with lattice vibrations in highly anisotropic polar materials. However, the lack of single-crystal thin film growth techniques limits further advancement of α-MoO_3. In this work, we describe a process for the growth of ultra-large, thin, and atomically smooth single crystals of α-MoO_3 directly on *a*-plane sapphire using an alkali-assisted physical vapor transport method. Important parameters necessary for high-quality growth to be discussed include substrate selection, alkali-to-MoO_3 ratio, and substrate temperature. The growth proceeds through a vapor-liquid-solid (VLS) mechanism enabled by the formation and liquefaction of low-melting point alkali molybdate phases. This growth mode greatly enhances lateral expansion to several millimeters and thicknesses ranging from hundreds of nm down to <5 nm. This is far thinner and more expansive than crystals grown without alkali metal additives, which can exceed several micrometers in thickness while being limited to a few tens of micrometers in lateral dimensions. The thin alkali-assisted sheets exhibit clean step-flow growth without grain boundaries over mm-scale areas as revealed by atomic force microscopy and polarized optical microscopy. Raman spectroscopy and X-ray diffraction indicate the high crystalline quality of the α-MoO_3 films rivaling that of accessible bulk crystals. We will also investigate the propagation of hyperbolic phonon polaritons using scanning near-field optical microscopy (SNOM) to compare hyperbolic phonon polariton lifetimes to values obtained from exfoliated bulk crystals. We find that this growth technique is suitable for exfoliation-free large-scale single-crystal α-MoO_3 for nanophotonics and other applications.

5:45pm **2D+EM+NS+QS+SS+TF-WeA-15 Studying the Impacts of Growth Temperature and Seeding Promoters on the Structural and Optoelectronic Properties of ReS_2 Grown by CVD***, **Elycia Wright**, Kedar Johnson, Amari Gayle, Robin Rouseau, M.K. Indika Senevirathna, Michael D. Williams,* Clark Atlanta University

Rhenium disulfide (ReS_2) is a fascinating member of the transition metal dichalcogenide (TMD) family, which has recently gained significant attention due to its distinct distorted octahedral 1T crystal structure characterized by triclinic symmetry. This distinctive structure shows that ReS_2 holds remarkable properties, including anisotropic electronic, optical, and mechanical characteristics. Unlike other TMDs such as MoS_2, $MoSe_2$, WS_2, and WSe_2, ReS_2 possesses a band structure that remains consistent regardless of the layer thickness. Due to weak interlayer coupling, it maintains a direct band gap in its bulk and monolayer forms. This unique characteristic makes ReS_2 particularly promising for applications in highly responsive photodetectors. To maximize the potential of ReS_2 for optoelectronic applications, it is essential to address the challenges associated with its anisotropic growth, distorted structure, and weak interlayer interactions. The anisotropic nature of ReS_2 can lead to variations in growth rates in different directions, resulting in multidomain structures that complicate the production of single-crystal ReS_2 on a large scale.

In this study, we will synthesize ReS_2 by chemical vapor deposition (CVD) at various temperatures and utilize seeding promoters to facilitate the growth of single crystals with continuous layers. We will employ advanced techniques such as confocal microscopy, Raman spectroscopy, and photoluminescence spectroscopy to systematically investigate how the growth temperature and seeding promoters affect the structural and optoelectronic properties of ReS_2.

6:00pm **2D+EM+NS+QS+SS+TF-WeA-16 Growth and Characterization of InSe Thin Films on GaAs(111)B and Si(111)***, **Maria Hilse**,* Penn State University

Urgent societal and environmental needs have sparked searches for high-mobility 2D materials with sizeable bandgap and decent stability under ambient conditions for use in ultra-low power, ultra-high performance field effect transistors. With a carrier mobility exceeding 1000 cm^2/Vs, small electron effective mass, flat electronic band dispersions, excellent optoelectronic, possible ferroelectric properties and a close-to-ideal solar spectrum matched bulk bandgap of 1.26 eV, InSe shows high potential for future use in electronics. Due to the layered nature, and the many members of different polytypes in the InSe materials family, intriguing confinement phenomena and exotic electron-hole coupling mechanisms tunable by the number of single layers add to the potential wealth of properties in InSe.

In this study, InSe thin films were grown by MBE on GaAs(111)B and Si(111). The presence of many InSe phases required a systematic mapping of the growth parameters to identify conditions for single-phase, single-polytype, and single-crystal growth. Through structural characterization in- and ex-situ using reflection high-energy electron and X-ray diffraction, growth conditions for solely gamma-phase, crystalline InSe films were found. Although the structural properties of the films presented nearly unchanged over a small window of growth conditions, the film morphology was seen to sensitively depend on the Se:In flux ratio. Raman spectroscopy confirmed the phase and polytype assignment deduced from large-area structural characterization.

Microstructure analysis, however, revealed a high degree of structural defects in the films. Nano-scale domains of varying single layer stacking sequences, high-angle rotational domains as well as single layers of unusual bonding configuration resulting in a novel InSe polymorph were found in the films. The total number of defects and the general locations of the new polymorph varied in films across GaAs and Si. The highest structural homogeneity was found for InSe films grown on Si.

Density functional theory calculations for a representative selection of the experimentally observed defects confirmed that most defects, including the novel polymorph have formation energies at or below the thermal budget of the MBE synthesis process. Although the bandgaps of all InSe polytypes and polymorphs possess comparable values, large differences were found in their relative offsets. Due to the random distribution of polytypes and polymorphs in the film, our study suggests a high degree of electronic disorder in these films. Electrical transport showed a variable-range hopping-like behavior supporting the hypothesis of electronic disorder.

Surface Science
Room 209 CDE W - Session SS-WeA
Heterogeneous Catalysis II

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, **Dan Killelea**, Loyola University Chicago

2:15pm **SS-WeA-1 "Single-Atom" Catalysis: Insights From Model Systems***, **Gareth Parkinson,*** TU Wien, Austria **INVITED**

Despite numerous successful syntheses and applications of single-atom catalysts (SACs), a fundamental gap persists between experimental approaches and theoretical modeling. Real-world catalysts are typically supported on complex powders and exposed to dynamic environments rich in potential ligands and contaminants. In contrast, density functional theory (DFT) calculations often rely on idealized models, such as low-index crystal facets and bulk-like atomic sites, which can oversimplify the real catalytic environment.

Model systems based on single-crystalline supports prepared under ultra-high vacuum (UHV) conditions offer a valuable bridge between theory and experiment. These well-defined systems provide a testing ground to validate theoretical assumptions and gain atomistic insights into catalyst-support interactions.

As a case study, I will present experimental results on iron oxide surfaces—materials widely studied in SAC literature due to reports of high catalytic activity for metal adatoms on FeOx. Notably, many DFT studies adopt the hematite (α-Fe_2O_3) (0001) surface as a model, though its atomic-scale structure remains complex and contentious. Instead, we investigate the $(1\bar{1}02)$ facet of hematite, which presents a stable, bulk-truncated (1×1) termination ideal for fundamental studies.

Our results demonstrate the adsorption behavior of Ir, Pt, and Rh single atoms on this surface. Crucially, stabilization of these atoms never occurs through simple adsorption at bulk-continuation sites. Instead, it involves either coadsorption of ligands or significant restructuring of the support itself—mechanisms that need to be accounted for in theoretical models of SACs.

2:45pm **SS-WeA-3 Ligand-coordinated Supported Catalysts for Selective Hydrocarbon Chemistry***, **Steven Tait**[1],* Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group has applied principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Initial studies were conducted on model surfaces under ultrahigh vacuum conditions.

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[1] **JVST Highlighted Talk**

Precise deposition control allowed for exploration of metal-ligand complexation requirements that would lead to highly stable 1D and 2D architectures. Reaction selectivity was tested by small exposures to reactive molecules. These systems provided models that have been adapted to high surface area supports under ambient conditions. Modified wet impregnation methods allow for loading of single-atom catalysts on high surface area powders at up to 1 wt%. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and X-ray absorption spectroscopy, electron microscopy, and CO adsorption measurements demonstrate single atom character of the catalysts. These ligand-coordinated supported catalysts have been shown to be effective for a variety of reactions, including hydrosilylation, hydrogenation, dehydrogenation, and water-gas shift. Here, we examine the significant roles of the coordinating ligands and of the oxide support on catalyst structure, activity, and stability. Defect sites on the support and the expressed facets of the oxide have a strong influence on the state of the metal centers and show a significant impact on reaction activity. We also see strong influences due to changing functional group substituents in the ligands. Synthetic routes have been developed to incorporate carboxylic acid groups into the ligand framework to increase metal-ligand and metal-surface interactions. We compare this with systems involving co-ligand deposition. By loading the metal and ligand directly on the oxide support, it is possible to maintain a close contact of the metal to the oxide. These results provide new insights into the design and chemistry of supported single-atom catalysts.

3:00pm **SS-WeA-4 Ethanol Oxidation over Single-atom Model Rh/Fe_3O_4(001) Catalysts**, ***Daniel Baranowski,*** Physical and Computational Sciences Directorate and Institute for Integrated Catalysis, Pacific Northwest National Laboratory

The selective oxidation of alcohols like ethanol, a renewable feedstock, is of pivotal interest, both from a fundamental and industrial perspective.[1] Inspired by previous ultra-high vacuum studies performed on model single-atom Pd/Fe_3O_4(001) catalysts activating the low-temperature methanol to formaldehyde oxidation,[2] a series of model Rh/Fe_3O_4(001) catalysts were examined for the low-temperature ethanol to acetaldehyde oxidation. Distinct Rh active sites, including Rh adatoms, substitutional in-surface Rh, and Rh clusters, were prepared using different preparation conditions and amounts of Rh.[3] The catalyst structures and activities were characterized by combining thermal desorption and photoelectron spectroscopies, and it was found that all model catalysts significantly reduce the temperature of the acetaldehyde production when compared to the bare Fe_3O_4(001) surface. There are, however, significant differences in the selectivities, not just between Rh single-atoms and clusters but also among the different single-atom species. The activity of all model systems was further tested during the presence of carbon monoxide. Surprisingly, the so far rather inactive in-surface Rh atoms turned out to exhibit promising properties when it comes to the upgrading of oxygenates.

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3:15pm **SS-WeA-5 Structure of Chemisorbed 1,3-Butadiene on the Cu(111) Surface and Its Influence on Selective Hydrogenation on a Pd/Cu(111) Single-Atom-Alloy**, ***Mohammad Rahat Hossain,*** *Michael Trenary,* University of Illinois - Chicago

The selective hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) is essential for refining alkene streams in high-quality polymer production. Traditional catalysts such as Pd and Pt exhibit nearly barrierless H_2 activation but suffer from CO-induced coking and excessive activity, which lowers selectivity. Single-atom alloy (SAA) catalysts, such as Pd/Cu(111), offer a promising alternative by leveraging the selective properties of Cu while maintaining Pd's hydrogenation activity. We investigated BD adsorption and hydrogenation on Cu(111) and a Pd/Cu(111) SAA using reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and density functional theory (DFT). TPD and RAIRS studies reveal that BD adsorption on Cu(111) exhibits intermediate interaction strength—more substantial than physisorption on Ag(111) and Au(111) but weaker than chemisorption on Pd(110) and Pt(111). Unlike strongly reactive surfaces that induce BD dissociation upon heating, BD desorbs intact from Cu(111). DFT analysis suggests that BD adopts both di-π and tetra-σ chemisorbed configurations on Cu(111). Over a Pd/Cu(111) SAA, ambient-pressure hydrogenation experiments indicate a first-order reaction (1.12 ± 0.03) for H_2 and zero-order (-0.12 ± 0.01) for BD, with a turnover frequency of 36 s^{-1} at 380 K and an activation energy of 63.2 ± 2.8 kJ/mol. Complete BD conversion is achieved with 84% selectivity toward 1-B without butane formation. TPD in ultrahigh vacuum (UHV) shows that monolayer BD desorbs at 217 K. In contrast, multilayers desorb between 112 and 180 K. No surface-bound intermediates are detected during reaction conditions. Post-reaction Auger electron spectroscopy (AES) reveals no carbon deposition, indicating no BD dissociation. These findings provide insights into BD adsorption and selective hydrogenation mechanisms on Cu-based catalysts, with implications for improving alkene purification strategies.

3:30pm **SS-WeA-6 Well-Defined Cu-Delafossite Catalysts**, ***Dario Stacchiola,*** Brookhaven National Laboratory

Cu-based catalysts are active for partial and full oxidation reactions. Deciphering the local atomic environment and oxidation state of active centers in supported copper catalysts, as well as the design of materials to control their stability under reaction conditions remains a great challenge. We show here that mixed-oxides of copper delafossites with gallium, aluminum or iron ($CuMO_2$, Cu^{1+} and M^{3+}; M: Ga, Al, Fe) in the form of porous nanoplates and films are promising materials as model catalysts to explore the activity and stability of Cu^{1+}-activated reactions. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

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"$CuGaO_2$ Delafossite as a High-Surface Area Model Material for Cu^+ Activated Reactions"

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"PLD of Delafossite Oxide Thin Films on YSZ (001) Substrates as Solar Water Splitting Photocathodes"

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4:15pm **SS-WeA-9 Formation of Monodispersed Palladium–Tellurium Nanoclusters on WTe_2(001): The Role of Excess Tellurium and Water**, ***Zdenek Dohnalek,*** Pacific Northwest National Laboratory **INVITED**

Understanding how metals and adsorbates interact with transition metal dichalcogenides is crucial for next-generation electronic, quantum, and catalytic applications. In this work, we explore palladium deposition on WTe_2(001) to reveal how mobile excess tellurium drives the formation of uniform, thermally stable $PdTe_x$ nanoclusters. Surprisingly, these clusters assemble independently of intrinsic surface defects. Upon annealing, they adopt identical size and structure, remaining stable up to ~500 K. Further investigation reveals that, contrary to common belief, the surface defects are hydroxylated rather than bare Te vacancies. The hydroxylation results from the adsorption and dissociation of background water, even under ultrahigh vacuum conditions. Density functional theory modeling supports these observations, explaining both the preferential nucleation of $PdTe_x$ clusters and the passivation of defects via water dissociation. These findings highlight how excess chalcogen atoms and water adsorption steer metal deposition, offering new pathways for creating robust, monodisperse nano-alloy structures for advanced quantum devices, microelectronics, and catalysts.

4:45pm **SS-WeA-11 Thermally Driven Chemical and Morphological Transition of Nb2O5 to NbO**, ***Jasper Brown,*** *Van Do, Steven Sibener,* University of Chicago

The structure and morphology of niobium surfaces plays a crucial role in the performance of superconducting radiofrequency (SRF) cavities, particle accelerators, and other advanced technological applications that require high-purity and low-defect materials. The presence of a native Nb_2O_5 oxide layer on Nb and anodized Nb surfaces introduces irregularities that can negatively influence superconducting properties, necessitating precise control over oxidative states. In this study, the dissolution-driven modification of Nb and anodized Nb surface roughness associated with the thermal reduction of Nb_2O_5 under high-temperature vacuum annealing conditions is examined. Using *in-situ* atomic force microscopy (AFM) the topographical evolution of Nb surfaces before and after oxide dissolution is characterized and changes in roughness at the nanoscale are quantified. Additionally, *in-situ* X-ray photoelectron spectroscopy (XPS) is employed to confirm the alteration of the surface oxide from Nb_2O_5 to NbO, providing insights into the chemical state evolution that drives this transformation. By systematically varying heating rates, annealing temperatures, and annealing times, the specific thermal and temporal conditions necessary to achieve the transition from pentoxide to monoxide are determined.

5:00pm **SS-WeA-12 Size and Support Effects on Propanol Electro-Oxidation Catalyzed by Sub-Nano, Size-Selected Ptn Clusters***, **Zihan Wang**, Lokesh Saravanan, Ratul Khan, Thaylon Hernandez, Scott Anderson,* University of Utah

The electrocatalytic oxidation of 1-propanol and 2-propanol by size-selected Pt_n clusters supported on indium tin oxide (ITO) and highly oriented pyrolytic graphite (HOPG) has been investigated. Pt_n clusters are generated and mass selected in the gas phase, then soft landed (~2 eV/atom) onto electrode surfaces prepared in UHV with controlled surface chemistry and defect density. After deposition, samples are transferred into a load-lock chamber, where aqueous electrochemistry can be carried out without air exposure. Electrochemical activity is evaluated using cyclic voltammetry (CV), and the cluster size and support effects are analyzed in combination with X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM).

We find that both the activity and selectivity for propanol oxidation depend on Pt_n size and the support surface structure. Furthermore, catalytic activity correlates with Pt core-level binding energies measured by XPS, suggesting that electronic structure is tuned by the cluster size and the support.For each support, activity varies with cluster size; overall, clusters supported on HOPG exhibit higher activity than those on ITO. In addition, the activity depends strongly on the ITO surface composition, which was varied by sputtering with Ar and annealing in O_2. For HOPG, the problem is that the weak Pt-HOPG binding leads to facile sintering, and atomic anchors such as nitrogen or titanium atoms are implanted to stabilize the clusters.The effects of the anchors on both electrochemical activity and stability, and on the cluster electronic properties will be discussed. This work is supported by the NSF Center for Synthetic Organic Electrochemistry (CHE-2002158).

5:15pm **SS-WeA-13 Adsorption of Carboxylic Acids and Reaction-driven Morphological Changes on the Fe3O4(001) Surface***, Jose Ortiz-Garcia*[1]*, Marcus Sharp, Benjamin Jackson, Mal Soon Lee, Peter Rice, Bruce Kay, **Zbynek Novotny**, Zdenek Dohnalek,* PNNL

Understanding the adsorption and conversion of carboxylic acids, such as formic acid and acetic acid, on oxide surfaces, including the cleavage of their C-O and C-H bonds, is essential for understanding CO_2 reduction and C-C coupling reactions. Formate acts as a key intermediate in CO_2 hydrogenation, while acetate serves as a crucial reactant in C-C coupling ketonization reaction. To unravel the catalytic activity and mechanistic details of these reactions, it is crucial to understand the interactions of carboxylic acids with model catalytic systems. We investigate the adsorption and reactions of formic acid (FA) and acetic acid (AA) on Fe_3O_4(001) using STM, XPS, LEED, and TPD. On the pristine surface, a $(\sqrt{2}\times\sqrt{2})$R45° reconstruction is observed, attributed to subsurface cation vacancies. FA and AA adsorb dissociatively, forming bidentate species and surface hydroxyls. At room temperature, both fully saturate the surface, exhibiting (1×1) periodicity from ordered bidentate species and hydroxyls, and (2×1) from distinct monolayer packing. Differences emerge upon annealing. For FA, annealing to 500 K leads to a rearrangement to the lowest energy (1×1) configuration, while at 600 K, partial recovery of the surface reconstruction and potential formation of single oxygen vacancy defects occur. Increasing the temperature to 700 K results in complete conversion of formate species and the formation of extended pits along the Fe rows. In contrast, AA shows stability up to 450 K without considerable morphological changes. Conversion begins at 550 K, with significant surface etching occurring at 650 K, leading to an irregularly pitted surface primarily elongated along the Fe rows. In comparing total etching for both molecules, AA leads to significantly more at approximately 21% of the surface area while FA etches only 3.3% of the surface. Higher etching for AA stems from additional hydrogen atoms leading to more H_2O formation via the Mars-van Krevelen mechanism and nonstoichiometric formation of CO_2 and CO, resulting in extensive pitting. Complete surface recovery is achieved via oxygen annealing at 930 K. To further understand the nature of the etch pit structures formed by these carboxylic acids, we employed density functional theory calculations, which provided insights into the atomic-scale structure of the etch pits. Simulated STM images closely align with experimental observations, reinforcing our understanding of the structural characteristics of the etched regions. Our findings highlight the importance of understanding carboxylate interactions with oxide surfaces, which is crucial for overcoming kinetic barriers in reaction pathways.

5:30pm **SS-WeA-14 Oxidation of a Rh(111)/(322) Bisected Crystal***, **Maxwell Gillum**, Alexis Gonzalez, Elizabeth Serna-Sanchez, Allison Kerr, Stephanie Danahey,* Loyola University Chicago*; Arved Dorst, Johhanes Dietrich,* Georg-August Universität, Göttingen, Germany*; Tim Schäfer,* georg-August Universität, Göttingen, Germany*; Dan Killelea,* Loyola University Chicago

Metal-catalyzed oxidation reactions are a major application of heterogeneous catalysis and are a widely applied synthetic route for the production of chemicals and reagents essential to modern society. The studies herein further investigate the influences that step density has on the formation of oxygen-induced surface reconstructions, linking lab-based single crystal studies to the high defect density surfaces present in industrial catalysis. The experiments focus on gaining structural information about the oxygen species present on the surface of a Rh(111)/(322) bisected crystal under various oxidative conditions utilizing low energy electron diffraction (LEED). These techniques are used in unison with temperature programmed desorption (TPD) and Meitner-auger electron spectroscopy (MAES) to identify optimal conditions for further study. We found that the (322) facet of the surface shows presence of oxide formation under oxidative conditions that are not aggressive enough to form oxide on the flatter (111) Rh surface. This indicates that the step edges play a much larger role in the formation of oxide on the Rh surface than previously thought.

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[1] **JVST Highlighted Talk**

2D Materials
Room 208 W - Session 2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM

2D Materials: Optoelectronics and Moire Excitons

Moderator: Daniel Yimam, Oak Ridge National Laboratory

8:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-1 Probing the Ultrafast Charge Dynamics and Exciton Emission from Single Atomic Defects in 2D Semiconductors by Lightwave-Driven STM***, Laric Bobzien, Lysander Huberich, Jonas Allerbeck, Eve Ammerman, Nils Krane, Andres Ortega-Guerrero, Carlo Pignedoli, Oliver Gröning,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Joshua A. Robinson,* The Pennsylvania State University*; **Bruno Schuler,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Two-dimensional (2D) semiconductors provide an exciting platform to engineer atomic quantum systems in a robust, yet tunable solid-state system. This talk explores the intriguing physics of single point defects in transition metal dichalcogenide (TMD) monolayers, investigated through atomically resolved scanning probe microscopy.

We have determined the layer-dependent charge transfer lifetimes of selenium vacancies in WSe$_2$ on graphene substrates, spanning picosecond to nanosecond timescales [1]. By leveraging our recently developed lightwave-driven scanning tunneling microscope (THz-STM) [2,3], we could probe the ultrafast charge dynamics on the atomic scale. Time-domain sampling with a THz pump-THz probe scheme enabled capturing atomic-scale snapshots of transient Coulomb blockade, a hallmark of charge transport mediated by quantized defect states [4].

Moreover, the extended charge state lifetimes provided by hBN decoupling layers facilitated the local, electrical stimulation of excitonic emission from pristine MoS$_2$ and individual charged defects via STM luminescence (STML).

By combining the structural and electronic properties accessible by conventional scanning probe microscopy with the optical fingerprint from STML and the excited-state dynamics revealed through pump-probe THz-STM, we gain a comprehensive microscopic understanding of localized quantum states in low-dimensional materials.

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8:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-3 Many-Body Effects on Excitons, Trions, and Defect-Bound States in 2D Materials***, **Kai Xiao,** Taegwan Park, Alexander Puretzky,* Oak Ridge National Laboratory, USA*; Xufan Li,* Honda Research Institute*; Kyungnam Kang,* Oak Ridge National Laboratory, USA*; Austin Houston,* University of Tennessee, Knoxville*; Christopher Rouleau, David Geohegan,* Oak Ridge National Laboratory, USA

Two-dimensional (2D) materials, particularly transition metal dichalcogenides (TMDs) exhibit strong many-body interactions due to reduced dielectric screening and spatial confinement. These interactions, involving electrons, holes, excitons, phonons, and plasmons, give rise to emergent phenomena distinct from their bulk counterparts. In this talk, I will present our recent investigations into the many-body effects on the optical properties and ultrafast excitonic dynamics of monolayer and bilayer TMDs. Specifically, we synthesized isotopically pure monolayer MoS$_2$ and highly defective WS$_2$ via nonequilibrium chemical vapor deposition, enabling a controlled study of isotope effects, defects, and background doping on excitonic behavior. Using ultrafast laser spectroscopy and temperature-dependent optical spectroscopy, we observed pronounced many-body interactions, including exciton-phonon and exciton-electron coupling, which significantly influence exciton energy, dynamics, and light-matter interactions in both monolayer and bilayer TMDs. These strong interactions give rise to novel quantum states and make 2D materials promising platforms for next-generation optoelectronics, quantum information technologies, and fundamental condensed matter physics.

Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

8:45am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-4 Proximity-Induced "Magic" Raman Bands in TERS Spectra of MoS2 / WS2 @ 1L H-BN-Capped Gold***, **Andrey Krayev,*** HORIBA Scientific*; Pavel Valencia Acuna,* PNNL*; Ju-Hyun Jung,* Pohang University of Science and Technology (POSTECH), Republic of Korea*; Cheol-Joo Kim,* POSTECH, Republic of Korea*; Andrew Mannix,* Stanford University*; Eleonora Isotta,* Max Planck Institute for Sustainable Materials, Germany*; Chih-Feng Wang,* PNNL

Recently it was proposed to use the monolayer h-BN – capped gold substrates as an ideal platform for the gap mode TERS and TEPL imaging, that on the one hand, should preserve strong gap mode enhancement of Raman signal due to small thickness (0.3 nm) of the dielectric h-BN layer, and on the other hand preserve strong TEPL response due to de-coupling of 2D semiconductors from the metallic substrate. TERS data collected on mono- and a few-layer-thick crystals of MoS$_2$ and WS$_2$ on 1L-h-BN-capped gold show both the TERS and TEPL response, confirming the validity of the proposed approach.

In addition to the enhancement of both the PL and Raman signal, in the course of assessment of TERS/TEPL response of mono- and a few-layer-thick crystals of MoS$_2$ and WS$_2$ deposited on 1L h-BN-capped gold we observed in TERS spectra, completely unexpectedly, appearance of Raman bands at about 796 cm^{-1} and 76 cm^{-1} which are not normally observed in regular Raman spectra of h-BN or WS$_2$/MoS$_2$. We can safely state that these "magic" bands belong to h-BN as they appear at the same spectral position in TERS spectra of both the monolayer MoS$_2$ and WS$_2$ deposited on the monolayer h-BN capped gold, moreover, the 796 cm^{-1} band often was the strongest band observed in TERS spectra, even stronger than A' mode from WS$_2$ or MoS$_2$. Presence of the transition metal dichalcogenide (TMD) monolayer is mandatory for the appearance of these "magic" bands as they are absent outside of the monolayer TMDs in these samples. Literature search showed that similar (but not identical) phenomenon was observed earlier in h-BN encapsulated WSe$_2$,MoSe$_2$, and WS$_2$. There have been several significant differences between our data and the earlier reported one: in our case we have not been able to observe the "magic bands" in MoSe$_2$ and WSe$_2$ @ 1L h-BN@Au, while WS$_2$ monolayers deposited on the same substrate as WSe$_2$, showed expected response. More importantly, the excitation laser wavelength dependence in our case was completely different from what was reported earlier: in WS$_2$-based samples we observed strong "magic" bands with excitation at 830 nm, 785nm, 594nm, but not 633nm, the wavelength closest to the A exciton in this material. This excitation profile is remarkably reminiscent of the excitation profile of the monolayer WS$_2$ in intimate contact with silver where we observed strong dip of the intensity of main A' mode in TERS spectra at 633nm excitation wavelength.

We will argue that intricate interaction between the tip-substrate gap plasmon, TMD excitons and most probably, normally mid-IR-active phonons in h-BN is responsible for the appearance of observed "magic" bands.

9:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-5 Correlated Excitons in TMDC Moiré Superlattice***, **Sufei Shi,*** Carnegie Mellon University **INVITED**

In a strongly correlated electronic system, Coulomb interactions among electrons dominate over kinetic energy. Recently, two-dimensional (2D) moiré superlattices of van der Waals materials have emerged as a promising platform to study correlated physics and exotic quantum phases in 2D. In transition metal dichalcogenides (TMDCs) based moiré superlattices, the combination of large effective mass and strong moiré coupling renders the easier formation of flat bands and stronger electronic correlation, compared with graphene moiré superlattices. Meanwhile, the strong Coulomb interaction in 2D also leads to tightly bound excitons with large binding energy in TMDCs. In this talk, we will discuss how to use optical spectroscopy to investigate excitonic physics and strongly correlated phenomena in TMDC moiré superlattice, along with correlated exciton states arising from strong interactions.

9:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-7 Sub-Stoichiometric Phases in 2D MoTe$_2$***, **Onyedikachi Alanwoko**, Nirosha Rajapakse, Matthias Batzill,* University of South Florida

Atom vacancy formation in crystalline materials is energetically expensive. To lower the energy cost for non-stoichiometry, point defects can condense into energetically more favorable extended defects. Studies on Mo-dichalcogenides have shown that excess Mo is condensed into closed, triangular Mirror Twin Boundary (MTB) loops. These MTBs can form in high densities where the triangular loops connect and form a cross-hatched network of MTBs. Here we show through Scanning Tunneling Microscopy (STM) that periodically ordered MTB networks can obtain a homologous series of sub-stoichiometric MoTe$_{2-x}$ phases. We systematically investigate the preparation conditions (which include a variation of the growth temperature, Te-desorption by post-growth annealing, and vapor-deposited Mo), enabling the controlled synthesis of these new phases. The different phases require different synthesis procedures, and once formed, these phases appear thermally stable in vacuum. The ability to control and create these different phases of $MoTe_2$ and other two-dimensional (2D) materials is a promising way of realizing new electronic and chemical properties of 2D materials. Particularly promising is the observation that we can react $MoTe_2$ with dissimilar transition metals to create new doped or alloyed 2D materials with potentially desirable properties.

11:00am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-13 Microwave Imaging of Excitonic States and Fractional Chern Insulators in 2D Transition Metal Dichalcogenides***, **Zhurun Ji**,* SLAC National Accelerator Laboratory/ MIT **INVITED**

Nanoscale electrodynamics offers a unique perspective on states with bulk-edge correspondence or spatially dependent excitations. I will introduce our latest advancements in optically coupled microwave impedance microscopy, a technique that enhances our capability to explore electrodynamics at the nanometer scale. I will discuss our recent studies utilizing this technology to extract spectroscopic information on exciton excitations within transition metal dichalcogenide systems. Additionally, I will share our recent findings on probing topological and correlated electronic states, specifically the fractional Chern insulator states in twisted TMD bilayers.

11:30am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-15 Control and Properties of Single Dislocations in Van Der Waals Nanowires***, **Peter Sutter**, Eli Sutter,* University of Nebraska - Lincoln

Line defects (dislocations) not only govern the mechanical properties of crystalline solids but they can also produce distinct electronic, thermal, and topological effects. Identifying and accessing this functionality requires control over the placement and geometry of single dislocations embedded in a small host volume to maximize emerging effects. We have identified a synthetic route that enables the rational placement and tuning of dislocation in van der Waals nanowires, where the 2D/layered crystal structure limits the possible defect configurations and the nanowire architecture puts single dislocations in close proximity to the entire host volume.[1] While homogeneous layered nanowires carry individual screw dislocations, the synthesis of radial (core-shell) nanowire heterostructures transforms the defect into a mixed (helical) dislocation whose edge-to-screw ratio is continuously tunable via the core–shell lattice mismatch.

Such deterministic control over defects now enables the probing of functionality arising with single dislocations. For example, germanium sulfide van der Waals nanowires carrying single screw dislocations incorporate Eshelby twist and thus adopt a chiral twisted structure,[2] which for the first time allowed the identification of chirality effects in the photonic properties of a single nanostructure.[3] Using cathodoluminescence spectroscopy, whispering gallery modes could be excited and probed to directly compare the photonics of chiral and achiral segments in single nanowires. The data show systematic shifts in energy, which with the help of simulations are assigned to chiral whispering gallery modes in wires hosting a single dislocation.

The ability to design nanomaterials containing individual dislocations with controlled geometry paves the way for identifying a broad range of functional properties of dislocations, with the potential to herald a paradigm shift from the traditional strategy of suppressing dislocations to embracing and harnessing them as core elements of new technologies.

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11:45am **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-16 Two-Dimensional Keldysh Theory for Non-Resonant Strong-Field Ionization of Monolayer 2D Materials***, **Tsing-Hua Her**,* UNC Charlotte*; Che-Hao Chang,* NTHU, Taiwan*; Kenan Darden,* UNC Charlotte*; Tsun-Hsu Chang,* NTHU, Taiwan*; Hsin-Yu Yao,* NCCU, Taiwan

Over the past decade, a diverse array of intense light interactions with monolayer two-dimensional (2D) materials have been reported, including low- and high-order harmonic generation (HHG), multiphoton absorption, optical injection of spin and charge currents, terahertz generation, and laser-induced dielectric breakdown. These processes are all initiated by interband transition of electrons induced by light with photon energy smaller than the bandgap energy. Some modeling efforts based on perturbation theory were attempted but their discrepancies with experiments are at least one order of magnitude, highlighting the lack of theoretical understanding of strong-field ionization in monolayer 2D materials. In this work, we report a new formalism of strong-field ionization for monolayer two-dimensional semiconductors based on 2D Keldysh (KLD) theory [T. -H. Her et al., Optica 12, 538-545 (2025)]. We take this approach because the original Keldysh theory [L. V. Keldysh, Soviet Physics JETP **20**, 8 (1965)] is the only theory that yields, for simplified band dispersion, analytical formulas for the cycle-averaged non-resonant ionization rate in bulk solids induced by a monochromatic electric field of arbitrary strength. It provides a smooth transition between multiphoton and tunneling ionization as what we now call the 'Keldysh parameter', , varies from >>1 to <<1. Due to their analyticity, Keldysh's formulas are widely employed for qualitative modeling of strong-field ionization in bulk solids. In this presentation, we generalize Keldysh's formulas to monolayer two-dimensional semiconductors. We derive closed-form formulas and their asymptotic forms for a two-band model with a Kane dispersion. We also derive selection rules related to the parity of multiphoton orders near the band edge. We validate our theory by comparing it to recent experiments and modeling of strong-field ionization in monolayer transition metal dichalcogenides (TMDs) with very good agreement (Figs. 1-3 of supplemental document) Specifically, our theory predicts a higher interband electron tunneling rate for 2D compared to 3D in the MIR frequency range, which successfully explains the 10x discrepancy (Fig. 3) between the experiment and modeling for HHG from monolayer TMDs [Liu et al., Nature Phys 13, 262–265 (2017)]. Considering the tremendous success of the original Keldysh theory in describing strong-field optical phenomena in atoms and solids, our 2D Keldysh theory is expected to find a wide range of applications in intense light-2D material interaction, such as optical limiting, multi-photon photodetection, THz generation through quantum interference, and photo-carrier doping for HHG.

12:00pm **2D+AQS+EM+MI+MN+NS+QS+SS+TF-ThM-17 Thickness Dependent Band Gap and Electrical Anisotropy of 2DSnSe***, Marshall Frye, Jonathan Chin, Joshua Wahl, Jeremy Knight,* Georgia Institute of Technology*; Walter Smith,* Purdue University*; Dilara Sen, Samuel Kovach,* Kenyon University*; Frank Peiris,* Kenyon College*; Charles Paillard,* University of Arkansas*; Thomas Beechem,* Purdue University*; Anna Osterholm, **Lauren Garten**,* Georgia Institute of Technology

2D SnSe presents unique opportunities for optoelectronics, and scalable microelectronics, but it is first critical to understand how the electrical and optical response change upon downscaling. Tailoring the band gap and electrical anisotropy of 2D monochalcogenides, like SnSe, has previously been shown but the mechanisms that drive the changes in band gap are still not understood. This study revealshow changes in bond length and structure drive the thickness dependences of band gap, carrier mobility and lifetime of SnSe thin films.Molecular beam epitaxy is used to deposit (2h00) oriented SnSe thin films with thicknesses ranging from 4 nm to 80 nm. The direct band gap increases from 1.4 eV at 80 nm to 1.9 eV at 4 nm, underscoring the potential of SnSe as a tunable and direct band gap material for thin film optoelectronics. Raman spectroscopy showsdifferent simultaneously changes in the crystal structure and bonding occurring parallel versus perpendicular to the 2D plane with decreasing film thickness. TEM further supports the hypothesis that the increase in the band gap with reduced thickness is due to changes in crystal structure resulting in a contraction of the out-of-plane SnSe covalent bonds, while the in-plane bond length increases. In addition to the reduction in band gap, tracking the time dependent photoluminescence shows an increase in carrier lifetime with decreasing film thickness, while Hall measurements show a change in the carrier mobility with decreasing thickness. Overall, this work provides the critical missing insight needed to design these optically and electronically relevant2D materials for scalability.

Surface Science
Room 209 CDE W - Session SS-ThM
Surface Electrical, Magnetic, and Optical Properties

Moderator: Melanie Müller, Fritz Haber Institute of the Max Planck Society

8:00am **SS-ThM-1 Storing and Processing Information in the Magnetic Quantum States of Single Surface Adsorbed Atoms***, **Harald Brune**,* Swiss Federal Institute of Technology Lausanne, Switzerland **INVITED**

The magnetic properties of single surface adsorbed atoms became one of the core interests in surface and nanoscience in 2003, where single Co atoms on Pt were reported to have 200 times the magnetic anisotropy energy of bulk Co [1]. Even 1000 times this energy was reached for single Co atoms on thin MgO films [2]. In a classical picture, this suggests that these single atoms should be rather stable magnets. However, despite numerous efforts, the magnetic quantum states of all investigated single surface adsorbed transition metal atoms had very short magnetic relaxation times, below 1 µs.

Immediately after changing from 3*d* elements to rare-earth atoms, a few adsorbate/substrate combinations could be identified, where the magnetization vector of a single atom is indeed stable over hours in the absence of an external magnetic field [3,4]. Therefore, these systems are single atom magnets and enable magnetic information storage in the smallest unit of matter. We will give an overview over the present adsorbate/substrate systems exhibiting single atom magnet behavior [3 – 10] and explain the essential ingredients for this surprising stability of single spin systems that are exposed to numerous perturbations from the environment. These atoms can be placed very close and still individually be addressed, conceptually enabling information storage at densities by 3 orders of magnitude larger than presently used devices.

Now the fundamental research field turns its attention to quantum coherent spin operations in single surface adsorbed atoms. If they have long enough coherence times with respect to the time it takes to perform a single quantum spin operation, these would be single atom quantum bits. The requirements for long coherence times of the magnetic quantum states are quite different from the ones of magnetic relaxation times. We will illustrate this with a few examples and point out single rare-earth atom systems that lend themselves already now as quantum repeaters in telecommunication [11], creating hope that single atom qubits may indeed become reality [12].

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8:30am **SS-ThM-3 Nonadiabatic Dynamics Simulations of Carbon Atom Scattering from Au(111)***, **Alexander Kandratsenka**,* MPInat, Germany

Measurements of energy loss spectra of carbon atom scattered off Au(111) surface conducted recently at Dalian Coherent Light Source facility suggest involvement of nonadiabatic effects. In order to construct a theoretical model describing that we are going to use the Independent-Electron Surface Hopping (IESH) approach, where the interaction of an incident atom (or molecule) with the surface induces the overlap of atomic and metallic orbitals facilitating energy exchange between projectile’s nuclear degrees of freedom and ehp of a metal. The first step here is to produce full-dimensional potential energy surfaces for each single-electron state relevant for the dynamics. In case of C atom, these are triplet (ground state) and singlet spin states of a neutral C, and quartet and doublet states of C anion. The second step is to perform nonadiabatic dynamics simulations to study the influence of Intersystem Crossing regions on the carbon atom energy loss spectra.

8:45am **SS-ThM-4 Oxidation of Ni-Based Superalloys: Closing the Gap from Adsorption to Microstructure***, William Blades,* Juniata College*; Keithen Orson,* University of Virginia, USA*; Juran Niu, Alexei Zakharov,* MAX IV Laboratory, Sweden*; Jerzy Sadowski,* Brookhaven National Laboratory*; **Petra Reinke**,* University of Virginia, USA

Ni-based superalloys are coveted for their corrosion resistance and formation of highly inert passive layers which limit degradation in a wide range of environments. Our work probes the oxidation process from the initial oxygen adsorption on a pristine alloy to the nanometer scale oxide layer using scanning tunneling microscopy and spectroscopy (STM/STS), and electron spectroscopies including X-ray photoelectron spectroscopy (XPS), and X-ray photoemission electron spectroscopy (XPEEM). We bridge the gap between single atom alloy to the complex solid solution surface, and realistic microstructure.

The Ni-Cr system has become a widely used model system for the study of oxidation, and passivity. It reflects the competition between Ni and Cr oxidation, the interplay between thermodynamic preference for chromia formation and kinetic limitations imposed by reactant transport in the alloy. The main factors which control the oxidation are alloy composition, temperature and crystallographic orientation. We will discuss the interplay between these factors on the oxide nucleation and growth between 200°C to 600°C with 5at% to 22at%Cr.

The delayed nucleation of NiO on Ni(100) is lifted on Ni-15Cr(100) leading to the rapid growth and step edge reconstruction with NiO. The chromia nuclei remain spherical due to their lack of epitaxial preference, although local segregation of Cr islands and a Cr(100)p(2´2) reconstruction is observed. Distinct variations in nucleation rate occur as a function of crystallographic orientation on Ni-15Cr(111) and several higher index surfaces on polycrystalline alloys. The direct observation of chromia nucleation on Ni-22Cr and Ni-22Cr-Mo with XPEEM opens the window to understanding the role of Mo, whose addition leads to high quality, chromia dominated, protective oxide layers. Adding Mo, or W modulates the surface chemistry towards chromia formation, and switches the growth to a layer-by-layer mode. Both, the barrier towards chromia formation, and the chromia-alloy interfacial energies are modified in favor of a dense protective layer.

A model which represents the alloy surface as a random solid solution will be used to capture adsorbate induced segregation as the initial step leading from adsorption towards oxide nucleation. The distribution of Cr in the surface is captured using fractal dimensions, percolation models and distribution functions combined with a systematic variation of diffusion constants for Cr. The outcome of the calculations is compared to nuclei densities and distributions from experiment.

9:15am **SS-ThM-6 Chemically Interrogating N-Heterocyclic Carbenes at the Single-Molecule Level Using Tip-Enhanced Raman Spectroscopy***, **Nan Jiang**,* University of Illinois - Chicago

N-heterocyclic carbenes (NHCs) have been established as powerful modifiers to functionalize metal surfaces for a wide variety of energy and nanoelectronic applications. To fundamentally understand and harness NHC modification, it is essential to identify suitable methods to interrogate NHC surface chemistry at the spatial limit. Here, we demonstrate tip-enhanced Raman spectroscopy (TERS) as a promising tool for chemically probing the surface properties of NHCs at the single-molecule scale. We show that with subnanometer resolution, TERS measurements are capable of not only unambiguously identifying the chemical structure of individual NHCs by their vibrational fingerprints but also definitively determining the binding mode of NHCs on metal surfaces. In particular, by investigating low-temperature NHC adsorption on Ag(111), our TERS studies provide insights into the temperature dependence of the adsorption properties of NHCs. Furthermore, we investigate the mobility of a model NHC on Ag(111). Two distinct molecular behaviors are observed, depending on substrate preparation. Room-temperature deposition leads to diffusing NHC–Ag adatom complexes exhibiting a ballbot-like motion, chemically identified by TERS through their spectroscopic fingerprint. By contrast, NHCs deposited at low temperature are stabilized on Ag(111) as isolated single molecules directly bound to the substrate. Significantly, a desorption/readsorption scenario is suggested for the displacement of NHCs by moving otherwise immobile single NHCs deposited at low temperature via STM manipulation, with their trajectory traced to atomic precision. This work suggests the potential of single-molecule vibrational spectroscopy for investigations of NHC surface modification at the most fundamental level.

9:30am **SS-ThM-7 Atomic-Scale Spectroscopy of Ultrafast Charge Order Dynamics in Charge-Density Wave Materials*, Sebastian Loth,*** University of Stuttgart, Institute for Functional Matter and Quantum Technologies, Germany **INVITED**

In materials with mobile electrons, electron-phonon coupling and electron-electron interaction can cause the emergence of charge-ordered phases, such as charge-density waves or Mott insula-tors. These ordered electronic states feature collective excitations that are absent in conventional metals but are fundamental to understanding correlated electron physics. By combining scanning tunneling microscopy with terahertz excitation (THz-STM) [1,2], we achieve simultaneous atomic spatial and femtosecond temporal resolution to directly visualize these dynamics at their intrinsic length and time scales.The extreme field enhancement at the STM tip apex produces localized THz fields reaching MV/cm [3]. This enables localized excitation of surfaces by the electric field of the THz lightwave through THz-induced Coulomb forces [4] and ultrafast screening currents. We apply this technique to two prototypical CDW systems: the incommensurate CDW in 2H-NbSe$_2$ and the commensurate CDW in 1T-TaS$_2$. In NbSe$_2$, we observe collective phase excitations at sub-THz frequencies that originate from atomic pinning sites, revealing how disorder dictates local dynamics and creates heterogeneity in the response [5]. In contrast, TaS$_2$ exhibits rapid reconfigurations within individual domains that show layer stacking dependence.These measurements demonstrate how ultrafast THz excitation at surfaces can manipulate electronic order in quantum materials with extreme spatial precision. This approach provides insights into the atomic-scale mechanisms governing CDW pinning. The ability to resolve these fluctuations in real space at the scale of individual impurities provides a new route to unraveling the electronic dynamics of disordered correlated materials. References:[1] Cocker., T. L., et al. *Nat. Photon.* 7 620 (2013). [2] Cocker., T. L., et al. *Nature* 539 7628 (2016). [3] Abdo, M., et al. *ACS Photonics* 8 702 (2021). [4] Sheng, S., et al. *Phys. Rev. Lett.* 129 043001 (2022).[5] Sheng, S., et al. *Nat. Phys.* 20 1603 (2024).

11:00am **SS-ThM-13 Measuring Properties of Single Defects, Dopants and Quantum Dots with nm Spatial Resolution*, Peter Grutter,*** McGill University, Canada **INVITED**

Semiconductor interfaces often have isolated trap states which modify electronic properties. We have developed a framework to quantitatively describe a metal-insulator semiconductor (MIS) device formed out of a metallic AFM tip, vacuum gap, and semiconducting sample. This framework allows the measurement of local dopant concentration, bandgap and band bending timescales with nm scale resolution of different types of defects on semiconductors such as Si, 2D MoSe$_2$ and pentacene monolayers [1].

With this method, we have characterize individual defects at the Si-SiOx interface. We show that surface charge equilibration timescales, which range from 1−150 ns, increase significantly around interfacial states [2]. We conclude that dielectric loss under time-varying gate biases at MHz and sub-MHz frequencies in metal-insulator-semiconductor capacitor device architectures is highly spatially heterogeneous over nm length scales. We have also analyzed two-state fluctuations localized at these interfacial traps, exhibiting bias-dependent rates and amplitudes. When measured as an ensemble, these observed defects have a 1/f power spectral trend at low frequencies [3]. Low-frequency noise due to two level fluctuations inhibits the reliability and performance of nanoscale semiconductor devices, and challenges the scaling of emerging spin based quantum sensors and computers. The presented method and insights provide a more detailed understanding of the origins of 1/f noise in silicon-based classical and quantum devices, and could be used to develop processing techniques to reduce two-state fluctuations associated with defects.

Force detection with single electron sensitivity can be used to perform localized electron energy level spectroscopy on semiconductor quantum dots, individual ferrocene molecules and atomically precisely positioned dopant atoms in Si. Single electron force spectroscopy allows the measurement of Coulomb blockade and eigen state energy levels, shell structure, excited state energies, coupling strength to electrodes, molecular vibrations, reorganization energies, electron-nuclear coupling (Franck-Condon blockade), stability diagrams (i.e. coupling between qdots) and double dot coherence time (for a recent review see [4]). I will describe the challenges and progress towards applying this single electron force spectroscopy technique to atomically precisely positioned quantum dots in Si.

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11:30am **SS-ThM-15 Activating Elastic Conformation of a Single Molecule via Qplus AFM Tip*, Markus Zirnheld,*** *A.M. Shashika D. Wijerathna, Yuan Zhang,* Old Dominion University

Mechanical properties of molecules adsorbed on material surfaces are increasingly vital for the applications of molecular thin films. In this study, we induce molecule conformational change on a single molecule through the application of mechanical load and quantify the associated force and energy required via a combination of a low temperature (∼ 5.4 K) ultra-high vacuum (~10^{-10} Torr) Scanning Tunneling Microscope (STM) and Qplus Atomic Force Microscope (Q+AFM). The molecule under investigation, TBrPP-Co (II) (a cobalt porphyrin), deposited on an atomically clean gold substrate, typically has two pyrrolic units (resembling pentagon rings) tilted upward and the other two downward. An atomically sharp Pt/Ir tip of the STM/Q+AFM, which vibrates with a high frequency (∼ 30kHz), is employed to run over a single TBrPP-Co(II) molecule at different heights with 0.1 Å as decrements and meanwhile to record tip-molecule interaction strength in the form of tip frequency change. When the tip approaches the threshold distance to the molecule, the mechanical load by the tip becomes large enough to trigger the elastic conformation of the molecule and cause pyrrolic units to flip their orientation in the opposite direction. Due to the sensitive nature of tip-molecule interaction, the pyrrolic units flipping can be directly visualized by STM, where upward-tilted pyrrolic units appeared as two bright protrusions, contrasting with the appearance of downward-tilted pyrrolic units. By processing frequency change, we obtain a three-dimensional mechanical force and potential maps for the single molecule TBrPP-Co(II) with the resolution of angstrom level. Our results indicate that a potential barrier of ∼ 49 meV is needed to activate the elastic conformational switch responsible for inducing pyrrolic units flipping of a single TBrPP-Co(II) molecule.

KEYWORDS

single molecular switch, mechanical load, qplus atomic force microscope, energy barrier, elastic conformational change, porphyrin molecule

11:45am **SS-ThM-16 Local Superconductor-to-Semiconductor Phase Transition in WS2 Controlled by STM Tip*, TeYu Chien*[1]*,*** University of Wyoming

Transition metal dichalcogenides (TMDs) are a unique class of materials that often host electronic correlation and strong spin orbital coupling. TMDs are two-dimensional (2D) layered materials with van der Waals (vdW) force between the layers allowing various stacking structures. Thus, TMDs often have polymorphic crystal structures, which exhibit drastically different physical properties. In WS$_2$, the most stable 2H phase is a topologically trivial semiconductor, while the metastable 2M phase is superconducting (SC) with critical temperature of 8.8 K. The 2M phase is also reported to be possible topological SC. A zero-bias peak has been reported inside magnetic vortices via scanning tunneling microscopy (STM) measurements and is considered to be a candidate of the Majorana Zero Modes (MZMs). It also has been reported that the metastable 2M phase WS$_2$ can be converted into 2H phase by heating. Thus, it is interesting to explore the possibility of creating topological SC anti-dot in nm scale to host the potential MZMs. In this study, we demonstrate a precise control of 2M to 2H phase transition in WS$_2$ using a STM tip “current pulsing” method. The resulting phase transition areas are notably sharply hexagonal following the 2H lattice orientation and can range from 30-350 nm in diameter. The effects of the electric field and tunneling current on the conversion will be discussed to provide insights of the conversion mechanism.

Funding acknowledgement: NSF OSI-2228841

12:00pm **SS-ThM-17 Multimodal Tool Combining Multichannel HREELS and ARPES/XPS to Study Electron-Boson Coupling*, Takahiro Hashimoto,*** *TImo Wåtjen,* Scienta Omicron AB, Sweden*; Xin Zhang, Andrew Yost, Daniel Beaton,* Scienta Omicron, Inc.*; Harald Ibach, Stefan Tautz, François Bocquet,* Forschungszentrum Jülich GmbH, Germany

Electrons in quantum materials couple to bosonic excitations, such as phonons and magnons, making it essential to characterize both these excitations and the electronic band dispersion. Multimodal

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[1] **JVST Highlighted Talk**

characterization, where a single sample is analyzed using multiple complementary techniques, offers a powerful approach to uncovering the interplay between various excitations and electronic structure. High-resolution electron energy loss spectroscopy (HREELS) is a technique for observing surface excitations including phonons, magnons, plasmons, excitons, and vibrational modes. Multimodal characterization has been difficult with a traditional single channel HREELS instrument because it requires its own detector, the measurements are time consuming, and angular resolution is limited. To improve the efficiency of HREELS measurements and to realize multimodal measurement with photoemission spectroscopy, we developed a solution by combining a monochromatic collimated electron source and a hemispherical electron analyser, commonly used for ARPES and XPS. The multichannel 2D detector of the analyser simultaneously measures hundreds of channels in both the energy and angular directions, and the measurements are orders of magnitude faster than the single channel setups. By adding a light source for photoemission spectroscopy, this setup becomes a multimodal characterization tool that combines state-of-the-art HREELS and ARPES/XPS using the same electron analyser. It allows to study the interplay between various surface excitations and electronic properties including electron-phonon coupling and electron-magnon coupling. Also, recent examples of HREELS measurements, including anisotropic exciton dispersion and topological phonons, are discussed to showcase the power of multichannel HREELS to observe novel excitations.

Surface Science
Room 209 CDE W - Session SS-ThA
Late Breaking Discoveries from the Rising Stars in Surface Science

Moderator: Nan Jiang, University of Illinois - Chicago

2:15pm **SS-ThA-1 Molecular Nanosystems at Interfaces*, Johannes Barth*[1]*,*** TU Munich, Germany **INVITED**

The utilization and organization of molecular species is an important issue for advancing nanoscale science and underpins the development of novel functional materials. To this end we explore molecular bonding and assembly at well-defined homogenous surfaces, textured templates, nanoelectrodes and 2D-sheet layers. The developed bottom-up fabrication protocols employ tailored building blocks and exploit both supramolecular engineering and on-surface covalent synthesis. Structure formation, chemical conversions, electronic and other characteristics are addressed by a multitechnique experimental approach, whereby scanning probe microscopy provides molecular-level insights that are frequently rationalised with the help of computational modeling. We work toward a rationale for the control of single molecular units and the design of nanoarchitectures with distinct functional properties.

3:15pm **SS-ThA-5 THz-Induced Metastability and Atomic-Scale Dynamics of Local Charge Order in 1T-TaS_2*, Melanie Müller*[2][3]*,*** Fritz Haber Institute of the Max Planck Society, Germany

Light-induced control of quantum materials has opened new frontiers in condensed matter physics, enabling the manipulation of electronic and structural phases on ultrafast timescales. While time-resolved pump–probe techniques provide insight into these dynamics, they typically lack the spatial resolution needed to probe atomic-scale variations arising from defects, heterogeneity, or domain boundaries.

Recent advances in ultrafast scanning tunneling microscopy (STM) have enabled real-space imaging of ultrafast dynamics with angstrom resolution. In particular, THz-lightwave-driven STM (THz-STM) has emerged as a powerful tool [1,2] for probing femtosecond carrier dynamics, molecular vibrations, and collective excitations at the sub-nanometer scale. However, applying THz-STM to quantum materials with easily perturbed ground states remains challenging, as it requires STM operation under intense localized THz fields that can strongly perturb the system. This is especially critical in layered materials such as 1T-TaS_2, where electron–phonon coupling, electron correlations, and stacking-dependent charge order render the system highly sensitive to external perturbations.

I will present THz-STM of the ultrafast dynamics of local charge order in the layered transition metal dichalcogenide 1T-TaS_2. At low temperatures, 1T-TaS_2 exhibits a commensurate charge density wave (CDW) phase with an insulating gap that arises from a complex interplay of electron correlations and interlayer orbital interactions. Starting from the C-CDW ground state, we demonstrate that THz excitation in the STM drives 1T-TaS_2 into a metastable state (MS) with a modified quasi-stationary insulating gap, which we assign to a THz-driven modification of the interlayer stacking order. On top, THz-lightwave-driven tunneling allows to probe the photoinduced dynamics of the collective charge order within the MS. In particular, coherent oscillations in the THz-driven tunnelling current reveal the 2.45 THz amplitude mode of the CDW, which persists in the MS. In addition, we find an unknown 1.36 THz mode that emerges near a local defect, which can be assigned to an interlayer shear mode which coherently modulates the interlayer orbital overlap and the low-energy states in 1T-TaS_2.

These results highlight the dual role of the tip-enhanced THz fields in THz-STM, both as a driver of metastability and for probing local ultrafast dynamics, and highlight the influence of defects on the dynamics of local charge order.

3:30pm **SS-ThA-6 Plasmonic Probes for Liquid-Phase Tip-Enhanced Raman Spectroscopy*, Naihao Chiang*[4][5]*,*** University of Houston

Tip-enhanced Raman spectroscopy (TERS) combines the chemical specificity of surface-enhanced Raman spectroscopy (SERS) with the unmatched spatial resolution of scanning probe microscopy (SPM). During the last few years, there has been an explosion of interest and activity in nanoscale vibrational spectroscopy. One of the key factors for successful TERS implementation is the quality of the plasmonic probes used. Electrochemically etched silver or gold tips are commonly used in scanning tunneling microscopy (STM) -based TERS, and sub-nanometer chemical mappings of single-molecule have been demonstrated under ultrahigh vacuum conditions.

We are developing plasmonic probes for scanning ion-conductance microscopy (SICM) and electrochemical STM (EC-STM) to extend TERS into the liquid phase. For SICM-TERS, quartz nanopipettes (<100 nm) were sputter-coated with silver or gold under high vacuum. SERS of small molecules directly tethered on the plasmonic nanopipettes were used to optimize the fabrication parameters. For EC-STM-TERS, electrochemically etched probes were coated with commercial ultraviolet (UV) cured polymers, aiming for a better chemical resistance and lower background signal compared to conventional nail-polish coatings. In the future, we expect these liquid-phase TERS probes to provide chemical information at interfaces relevant to the emerging catalysis, energy, and bioengineering applications.

3:45pm **SS-ThA-7 Surface Science Reception*,***

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[1] **Surface Science Keynote Lecture**

[2] **JVST Highlighted Talk**

[3] **Rising Star in Surface Science**

[4] **JVST Highlighted Talk**

[5] **Rising Star in Surface Science**

Surface Science
Room Ballroom BC - Session SS-ThP
Surface Science Poster Session

SS-ThP-1 Exploring the Oxidation State Void between Single-Atom Alloys and Single-Atom Catalysts: Insights from RhCu and PtCu Alloys*, **Vinita Lal**[1], E. Charles H. Sykes,* Tufts University

Our aim is to explore the phase space between single-atom alloys (SAAs) and single-atom catalysts (SACs), where both the support and the single-site species exist in a partially oxidized state. SAAs have been extensively studied for hydrogenation, dehydrogenation, and coupling reactions, with growing interest in their potential for selective oxidation chemistry. However, their behavior under oxidizing conditions remains less understood. Since oxidation plays a crucial role in numerous catalytic processes, uncovering how oxygen interacts with SAAs and influences their reactivity and selectivity is essential for expanding their applicability in oxidation reactions. By investigating these interactions, we aim to provide new insights into the catalytic potential of SAAs and bridge the knowledge gap between SAAs and SACs.

To achieve this, we use well-defined model systems to study oxygen-mediated reactivity in SAAs. We investigate the oxidation of RhCu(111) SAAs using iodomethane as a probe molecule to examine how pre-adsorbed oxygen affects C-H activation and C-C coupling on both Cu(111) and RhCu(111). Through temperature-programmed desorption (TPD) and density functional theory (DFT) modeling, we show that C-H activation is inhibited on oxidized RhCu(111) compared to Cu(111) and that product selectivity follows distinct trends on SAAs relative to Cu(111) as a function of oxygen coverage. Expanding this framework, we explore O_2 activation and methanol oxidation on the PtCu(111) SAA system. TPD, X-ray photoelectron spectroscopy (XPS), and DFT analyses reveal that Pt slightly inhibits Cu(111) oxidation, contrasting with the promoting effect of Rh single atoms. However, Pt does not significantly alter Cu's selectivity in methanol oxidation, highlighting the complex role of different single-atom species in oxidation chemistry.

By shifting the focus from traditionally studied reducing conditions to oxidized environments, this work deepens our understanding of SAA reactivity and provides a foundation for tuning single-site catalysts for selective oxidation reactions. Our findings contribute to a broader understanding of how SAAs operate under oxidizing conditions, offering insights that could help guide the design of catalysts with enhanced functionality for industrially relevant oxidation processes.

SS-ThP-2 Development and Application of an Optimized Photo-Assisted Metal-Assisted Chemical Etching for Overcoming Fabrication Challenges in GaN Schottky Diodes*, **Krystal Woodruff**,* Kyma Technologies

Gallium nitride (GaN) has come up as a highly promising semiconductor material due to its wide band-gap, high breakdown voltage, and excellent thermal properties, making it ideal for high-power, high-frequency devices. Metal-assisted chemical etching (MacEtch) offers an adaptable approach to patterning GaN by combining the anisotropic control typical of dry etching with the cost-effectiveness and lower sidewall damage associated with wet etching. In this study, Kyma GaN wafers were subjected to MacEtch with a variety of solution concentrations, temperatures, and etch durations. The resulting etched structures were characterized using techniques such as scanning electron microscopy, white light interferometry, and optical microscopy.

The findings revealed a clear relationship between MacEtch parameters and subsequent GaN etch rates and surface morphologies. When applied as a trenching technique to Schottky diode structures, moderately etched devices showed improved reverse breakdown voltage, as expected from the trench architecture over planar structures. Ultimately, the work demonstrates how MacEtch can be used as an alternative to dry etching, as well as its ability to be used as a trenching technique to enhance the blocking voltage performance of GaN-based Schottky diodes. With refined processes and careful control of environmental factors, MacEtch holds significant promise for advancing GaN device fabrication, particularly in high-power applications.

SS-ThP-3 Product Promoted Acetylene Cyclotrimerization to Benzene and Propyne-Acetylene Coupling to Toluene on Ag(111)*, **Nipun Kahagalla Dewage**,* Tufts University*; Santu Biswas,* Tulane University*; Dennis Meier, Volkan Çinar,* Tufts University*; Matthew M. Montemore,* Tulane University*; Charles Sykes,* Tufts University

Benzene (C_6H_6) and toluene (C_7H_8) are irreplaceable chemical feedstocks for various products ranging from pharmaceuticals to building materials. They are primarily produced through petroleum cracking and reforming, which require high energy input, severe operating conditions, and lack 100% selectivity. With the shift from oil to shale gas as a hydrocarbon feedstock, there is an interest in alternative methods to produce C_6H_6 and C_7H_8. One promising pathway is the cyclotrimerization of acetylene (C_2H_2), which uniquely achieves 100% selectivity to C_6H_6 on the Ag(111) surface. However, it requires more than a monolayer (ML) of acetylene to initiate the benzene formation, necessitating high reactor pressures that could limit its industrial feasibility.

In the first study, acetylene cyclotrimerization on Ag(111) was investigated using Temperature Programmed Desorption (TPD), 12 Kelvin Scanning Tunneling Microscopy (STM), and Density Functional Theory (DFT) to explore how 2D compression by the reaction product benzene affects reaction rate. Isotopically labeled benzene (C_6D_6) was used to investigate the coadsorption of benzene and acetylene. Our results demonstrate that coadsorbed benzene (1/3 ML C_6D_6) enhances acetylene conversion and lowers the threshold acetylene coverage from 1 ML to ~0.3 ML. Increasing C_6D_6coverage up to 1 ML further enhances acetylene conversion, whereas an increase beyond 1 ML reduces both conversion and benzene yield due to decreased surface site accessibility for acetylene. DFT calculations show that the presence of two parallel and slightly overlapping benzene molecules with two acetylene molecules on a 4×4 Ag slab has the lowest energy for the rate-limiting step of forming the C_4 reaction intermediate compared to other possible coadsorbed configurations. The local organization was further investigated by STM confirming similar molecular density of acetylene and benzene as used for the DFT calculations.

In our second study, C_2H_2 and C_3H_4 were coadsorbed to examine the coupling between C_2H_2 and C_3H_4 by TPD and DFT. C_2H_2 and C_3H_4 undergo coupling at a full monolayer of coadsorbed molecules. However, C_7H_8 is just a byproduct (~5%), while C_6H_6 remained the main product (95%). C_3H_4 does not couple with itself to form either benzene or trimethylbenzene on Ag(111), which aligns with the high reaction barrier for C_3H_4 self-coupling suggested by DFT due to sterics.

These findings provide fundamental insights into product-driven promotion of acetylene cyclotrimerization and hetero-coupling of C_2H_2 and C_3H_4 on Ag(111), informing strategies for catalyst design and identifying a new reaction pathway for toluene production.

SS-ThP-4 Ni Nanocluster formation and Intercalation in Graphene/Ir(111) Heterostructures*, **Shilpa Choyal**,* University of Illinois at Chicago*; Michael Trenary, Nan Jiang,* University of Illinois - Chicago

The interfacial engineering of graphene-metal heterostructures through atomic intercalation presents a powerful approach for modulating electronic properties while preserving graphene's structural integrity. This investigation examines the temperature-dependent evolution of transition metal nanoclusters on epitaxial graphene/Ir(111) surfaces, with emphasis on intercalation mechanisms and their effects on the electronic structure of graphene.

Using high-resolution scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED), we characterized the structural transformations occurring when Ni is deposited onto graphene/Ir(111) at various temperatures. The pristine graphene layer exhibits a characteristic moiré pattern with 2.5 nm periodicity, resulting from lattice mismatch between graphene and Ir(111). Upon metal deposition at ambient temperature, Ni nanoclusters demonstrate remarkable site selectivity, exclusively nucleating at fcc sites among three possible adsorption positions. At ambient temperature, these nanoclusters form triangular islands aligned with the substrate's close-packed directions, spanning multiple moiré units with lateral dimensions of 10-15 nm and vertical heights of 1.4 nm.

Thermal annealing at 900 K induces Ni intercalation between graphene and Ir(111), as evidenced by the disappearance of surface clusters and emergence of a reverse moiré pattern compared to graphene on Ir(111). After intercalation, atop sites appear as bright protrusions instead of depressions. For Ni intercalation, we observe two distinct moiré patterns which are round and clover-like in shape, arising due to intercalation under

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

two different adsorption sites. Upon further annealing to 1500 K, the intercalated metals adopt pseudomorphic growth on Ir(111), maintaining epitaxial registry despite significant lattice mismatch. This indicates substantial electronic interaction with both graphene and substrate. These insights advance the fundamental understanding of interfacial phenomena in two-dimensional materials and provide pathways for developing graphene-based electronic devices with tailored properties.

SS-ThP-5 Understanding Azide Modifications on Metal Oxides: A Window Into a New Class of Small Molecule Inhibitors*, **John Mason**, Andrew Teplyakov,* University of Delaware

Recent developments in area selective atomic layer deposition (AS-ALD) target requirements for smaller sized features as well as better control over surface chemical modification that governs the selectivity. This has brought attention to the use of small molecule inhibitors (SMIs) as a tool to assist in altering surface reactivity and thus enabling the miniaturization of these features. Azides are a common molecular species that has gained interest for surface modifications due to their non-reactive biproducts, nitrogen doping capabilities, and reactivity when brought into contact with a surface. This study aims to explore the reaction pathways for two different azides, trimethylsilyl azide and benzyl azide, and their reactions on metal oxide surfaces to see what conditions are needed to react with these surfaces, and what the surface species is afterwards. Using in-situ infrared spectroscopy and X-ray photoelectron spectroscopy we aim to observe the bonding configuration of these azide molecules on metal oxides and to explore the stability of the resulting surfaces as a pathway towards utilization of azides as SMIs.

SS-ThP-6 Surface Properties of Zirconium diboride (0 0 0 1) and Homoepitaxial Growth of Zirconium diboride as determined by Scanning Tunneling Microscopy*, Michael Trenary, **Ayoyele Ologun**[1],* University of Illinois - Chicago

Zirconium diboride, ZrB_2, a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C and can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride $Zr(BH_4)_4$ as a precursor. Using ultrahigh vacuum scanning tunnelling microscopy (STM), we investigated the atomic-scale structure of ZrB_2(0001) and the homoepitaxial growth of ZrB_2 on this surface.After exposures of $Zr(BH_4)_4$ to ZrB_2(0001) at 1473 K and immediately cooling to room temperature, Zr-terminated bilayer islands of ZrB_2 were observed. Coalescence of the ZrB_2 islands was observed when the substrate was left for 60 minutes at the deposition temperature before imaging at room temperature. In contrast, exposure at 900 K resulted in high-density clusters. Stepwise annealing at 1400 K led to the transformation of these clusters into a continuous thin film via thermal-induced coalescence.

SS-ThP-7 Comparing Computational Methods for Predicting STM Images*, **Kaitlyn Handy**, Alex Kandel,* University of Notre Dame

Scanning tunneling microscopy (STM) allows for an image to be constructed of a molecular surface. STM utilizes a tunneling current that interacts with the electronic density of states to produce a topographic image of a surface. With the knowledge of how these STM images are created, then theoretical predictions for molecular surface STM images can be produced and compared to experimental data to verify predicted molecular geometries.

There are two different methods for predicting STM images that are being investigated through this work. The first method calculates molecular electron density from gas-phase calculations. The STM images are then generated by varying the tunnel decay, current, and molecular orbitals. The second method is VASP; calculating the full electronic structure of the molecule in the presence of a surface to create a predicted STM image. This study aims to determine the conditions that the gas-phase STM images, which are computationally cheaper, are able to produce results comparable to VASP. Thus far, the accuracy of these images has been found to depend on molecular planarity and the orientation of the molecule relative to the surface.

SS-ThP-8 Investigation of sub-Nanoscale Light-Matter Interactions in Carbon Nanomaterials Using Tip-Enhanced Raman Spectroscopy*, **Yuto Fujita**[2],* Keio University, Japan*; Norihiko Hayazawa,* RIKEN, Japan*; Maria Vanessa Balois-Oguchi,* Institute of Science Tokyo, Japan*; Satoshi Yasuda,* Japan Atomic Energy Agency, Japan*; Takuo Tanaka,* RIKEN, Japan*; Tomoko K. Shimizu,* Keio University, Japan

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique for exploring novel optical phenomena, especially light-matter interactions at the nanometer scale [1]. It takes advantage of the near-field light generated at the apex of a sharp metallic tip. By utilizing the gap-mode between the tip apex and a metallic surface, spatial resolutions of approximately 1 nm [2] or even sub-nanometer resolution [3,4] can be achieved. In this study, we use a scanning tunneling microscope (STM)-based TERS system with sub-nanometer resolution in ambient conditions [4] to examine light-matter interactions in carbon nanomaterials under sub-nanometer scale light confinement in a working environment. While conventional far-field Raman spectroscopy of carbon nanotubes (CNTs) shows a weak D-band, typically attributed to defect-induced scattering, we found that TERS spectra revealed a significantly enhanced D-band, suggesting a different excitation mechanism. We propose that the high wavenumber of the near-field light preserves momentum conservation for electronic transitions associated with the D-band in TERS measurements, a role typically played by defects in conventional Raman scattering [5]. These findings highlight the unique effects of sub-nanoscale light confinement on electronic excitations in materials. Further discussions, including results for graphene, will be presented.

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SS-ThP-9 Localized Physical and Chemical Manipulation of Surfaces via Thermal Scanning Probe Lithography (t-SPL)*, **Nicholas Hendricks**, Emine Çağin,* Heidelberg Instruments Nano AG, Switzerland

Modification of thin film surfaces is of the utmost importance for various applications ranging from biosensors and spintronics to flat optics and magnonics. To push the performance of such applications to the next level, the optical, electrical, chemical, or magnetic properties need to be locally controlled at the sub-50nm length scale. To convert thin film surfaces, the use of direct-write lithography techniques is often employed where the film is manipulated by electrons, photons, or ions. These energetic particles can induce physical and chemical changes, however, the direct use of thermal energy as the stimulus could provide a more universal stimulus as well as an alternative route for such modifications. With thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor from Heidelberg Instruments, the use of heat to perform direct-write patterning conversions is possible [1-5].

t-SPL generates patterns by scanning an ultrasharp tip over a sample surface to induce local changes with a thermal stimulus. By using thermal energy as the stimulus, it is possible to perform various conversion processes such as functional surface group deprotection, precursor conversion, and crystallization. Along with an ultrasharp tip, with a radius less than 10nm, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor, a capacitive platform for electrostatic activation, and an integrated heating element. By having a cantilever with such properties, it's possible to generate 2D and grayscale chemical gradients where surface chemistry is critical.

In this presentation, the background and workings of t-SPL will be introduced along with the lithography and processing steps necessary to create chemical gradients through the deprotection of functional groups for enzyme and protein patterning. The patterning of a phase change material (PCM) of GeSbTe (GST) will also be discussed where sub-300nm phase changes have been optically observed.

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SS-ThP-10 Probing the Oxygen-Driven Metal-Support Interactions in Pt/TiO$_2$ with Near-Ambient Pressure Spectroscopy and Microscopy*, **Gaurav Anand**[1], Florian Kraushofer, Matthias Krinninger, Marina de la Higuera-Domingo, Lorenz Falling, Barbara A.J. Lechner,* Technical University Munich, Germany

Platinum supported on titanium dioxide (Pt/TiO$_2$) is a prototypical model system for studying redox reactions and understanding metal-support interactions in surface science studies for heterogeneous catalysis. The Pt/TiO$_2$ interface serves as a dynamic active site, and can modulate catalytic activity, particularly under mild reaction conditions. However, as we approach more realistic environments - where elevated temperatures and pressures introduce complex, intertwined interactions between the metal particles, the oxide support, and gas-phase species - more sophisticated experimental probes are required. For example, in oxidizing environments the behavior of Pt on rutile TiO$_2$ remains debated. While encapsulation via classical strong metal support interaction (SMSI) - where Pt is buried by a reduced TiO$_x$ (x < 2) overlayer[1] - has been well-documented in reducing conditions, recent observations suggest that oxidizing conditions can also lead to encapsulation via a "non-classical" mechanism.[2] In the latter scenario, a stoichiometric TiO$_2$ layer is observed to overgrow Pt, but the driving forces behind this phenomenon remain unclear, partly due to ill-defined defect densities within the oxide support.

We employ near-ambient pressure scanning tunneling microscopy (NAP-STM), X-ray photoelectron spectroscopy (NAP-XPS), and low-energy ion scattering (LEIS) to investigate the Pt/TiO$_2$(110) interface under oxygen pressures ranging from ultra-high vacuum (UHV) to 1 mbar. Our results reveal a strong correlation between the oxidation state of Pt, the stability of Pt nanoparticles, and the stoichiometry of the TiO$_2$ support.[3] Under low oxygen pressures and on reduced TiO$_2$ substrates, Pt nanoparticles become encapsulated by stoichiometric TiO$_2$ overlayers, likely driven by substrate reoxidation and the presence of metallic Pt, while the classical SMSI-driven TiO$_x$ (x < 2) overlayer remains unchanged. In contrast, at higher oxygen pressures, Pt nanoparticles exhibit increased resistance to encapsulation, potentially due to Pt oxidation.[4] Furthermore, on near-stoichiometric TiO$_2$ substrates, encapsulation is suppressed even at near-ambient oxygen pressures, allowing Pt nanoparticles to undergo oxidation instead. These findings provide new insights into the complex nature of metal-support interactions in oxidizing environments and offer a more nuanced understanding of Pt/TiO$_2$ catalysts under realistic reaction conditions.

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SS-ThP-12 Methanol Dehydrogenation on Pt / Cu (111) Single Atom Alloy Surface*, Michael Trenary, **Vishwa Don Lokugan Hewage**,* University of Illinois - Chicago

Pt/Cu(111) single atom alloys (SAAs) have been reported to catalyze the non-oxidative dehydrogenation of alcohols, selectively forming the corresponding aldehydes and hydrogen. They do so by facilitating O-H bond cleavage to form an alkoxy intermediate and C-H bond cleavage of the alkoxy to form the aldehyde. In this study, methanol dry dehydrogenation reactions on Pt/Cu(111) SAA surfaces were investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) to determine reaction intermediates and pathways. Although no formaldehyde desorption was observed from Cu(111), 0.02 ML of formaldehyde desorbs from a Pt/Cu(111) surface at 375 K. A RAIRS peak at 1005 cm^{-1} on the SAA surface, observed at 250 K, was assigned to the C–O stretching mode of methoxy, compared to the corresponding methoxy C–O stretching peak(1005 cm^{-1}) on an oxygen-pre-adsorbed Cu(111) surface. The methoxy yield (0.001 ML), estimated from the CO stretching peak area on the SAA surface, was lower than the number of Pt single atoms (0.04 ML), contrary to the expectation that a single Pt site could form multiple methoxy molecules via spillover onto Cu sites. To assess the effect of background CO, the formaldehyde yield was compared to an SAA surface where Pt sites were blocked by CO dosed at 250 K. The formaldehyde yield decreased by approximately 50%, confirming that background CO suppresses the reaction yield on the Pt/Cu (111) SAA surface. These findings provide insights into the mechanistic role of Pt sites in methanol dehydrogenation and the impact of surface species on catalytic efficiency.

SS-ThP-13 Automated Workflows in Photoelectron Spectroscopy: Enhancing Reproducibility and Efficiency*, **Jonathan Counsell**, Liam Soomary,* Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

The widespread application of X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) in materials characterization necessitates automation to improve workflow efficiency and analytical consistency. Reproducibility challenges, stemming from operator-dependent data processing and spectral interpretation, threaten the reliability and broader utility of these techniques. Automated data handling systems mitigate analyst bias, reduce errors, and enhance the comparability of results across different laboratories.

This work explores the implementation of automated workflows in XPS and UPS, focusing on large-area analysis, depth profiling, and data compilation. We examine key challenges such as X-ray-induced damage, transmission and analysis area calibration, surface uniformity, and quantification consistency. Case studies will highlight automated solutions for handling complex material systems, demonstrating the role of advanced data processing in standardizing spectral interpretation. Furthermore, we discuss recent developments in high-throughput XPS systems that incorporate automated spectral fitting, background subtraction, and large-scale data integration, improving data reliability and reducing manual intervention [1,2].

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SS-ThP-14 Single-Atom Cu-Embedded Mo$_2$Ct$_x$ Mxene for Selective Reduction of Co$_2$ to Methane*, **Dinushika Kotudura Arachchige**,* University of Florida, Gainesville

The electrochemical reduction of CO$_2$ (CO$_2$RR) is a promising approach to mitigating carbon emissions while generating value-added products under ambient conditions. However, achieving high selectivity and efficiency remains challenging due to the competing hydrogen evolution reaction (HER) and the strong correlation of binding energies among reaction intermediates. Single-atom (SA) catalysts, with their unique electronic properties, have emerged as promising candidates for CO$_2$RR. However, their performance is often limited to CO production at high overpotentials, and their stability is compromised due to atom aggregation.

MXenes, with their high surface electron density, provide a robust platform for stabilizing transition metal SAs, preventing aggregation under catalytic conditions. Herein, we report the design and synthesis of a Cu SA-embedded 2D Mo$_2$CT$_x$ MXene electrocatalyst for the selective reduction of CO$_2$ to methane (CH$_4$) at low overpotentials. The successful incorporation of Cu SAs into the 2D MXene sheets led to a high Faradaic efficiency (~94%) for CH$_4$ formation at low applied potential (~ -0.3 V vs RHE), with significant suppression of HER. This enhanced selectivity is attributed to the strong CO adsorption on Cu SAs via back-donation, prolonging its residence time and facilitating further hydrogenation through MXene surface functional groups.

SS-ThP-15 Kevion: An Ion Irradiation Facility for Transformative Research in Space Science at the University of Virginia*, **Adam Woodson**, Catherine Dukes, Aubrey Carley, Robert Johnson,* University of Virginia*; Jeroen Terwisscha van Scheltinga,* Leiden University, Netherlands*; John Ihlefeld, Petra Reinke, Robin Garrod, Ilsedore Cleeves,* University of Virginia

The KiloElectron Volt ION (KEVION) irradiation facility for space science — a new NASA Planetary Science Enabling Facility — is under development within the Laboratory for Astrophysics and Surface Physics at the University of Virginia (LASP-UVa). This user-focused facility, available at no cost to NASA Planetary Science Division (PSD) grantees, is comprised of four integrated components: (1) a 25–300 keV Pelletron ion accelerator to provide positive atomic or molecular ions over a wide range of species, charges, and energies; (2) a novel, new ultrahigh vacuum (UHV) chamber called "GRAINS" that incorporates X-ray photoelectron spectroscopy, mass spectrometry, hyperspectral imaging, and more for holistic studies of geologic samples and other materials; (3) an established, well-tested cryogenic UHV chamber, aptly named "ICE", for studies concerning the irradiation of condensed gas targets; and (4) a minimally equipped, user-

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configurable UHV chamber called "TEST" for instrument testing, calibration, and prototyping. The KEVION is expected to facilitate transformative research in space weathering, radiolysis, radiosynthesis, sputtering, radiation damage, surface charging, and instrument development/response testing.

A full-time facility instrument scientist is available to assist with experiment planning, instrument operation, instrument training, and data analysis. The KEVION facility will be fully operational by the end of 2025, though the GRAINS chamber chamber will be ready for use without the Pelletron by the summer of 2025. The facility will be accessible both in person and remotely. Specific details of the Pelletron accelerator and analytical techniques associated with each end chamber are summarized on the KEVION website at https://engineering.virginia.edu/kevion, and on the NASA Science Mission Directorate website at https://smd-cms.nasa.gov/wp-content/uploads/2023/06/KEVION.pdf.

Investigators submitting proposals to any of the NASA PSD funding programs are encouraged to integrate the KEVION facility into their research plans. We also welcome non-PSD academic, governmental, and industrial clients to make use of the facility at a nominal, tiered hourly rate. For more information email Cathy Dukes at cdukes@virginia.edu or Adam Woodson at akw8r@virginia.edu.

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SS-ThP-16 The Importance and Reporting of NAP-XPS Instrument Parameters*, **Braxton Kulbacki**[1], Joshua Pinder, Jacob Crossman, Matthew Linford,* BYU

X-ray photoelectron spectroscopy (XPS) data acquisition is directly affected by a variety of instrumental and software parameters. Accordingly, gaining a full picture and proper understanding of the material being analyzed and reported on, requires adequate reporting of these parameters. With recent advancements in XPS technique, XPS has become more commonplace. Although XPS is being used at an increasing rate, the number of XPS experts has not increased at the same rate. Thus, inadequacies in reporting are becoming more prevalent. A variant of XPS, called Near-ambient pressure XPS (NAP-XPS) is important because it allows data to be taken at much higher pressures than is done conventionally. Many samples that cannot be analyzed by conventional XPS can be analyzed by NAP-XPS. This poster examines parameter reporting within NAP-XPS – containing publication results from 2021 to 2023, highlighting gaps in parameter documentation. The reported parameters include the electronic analyzer (spectrometer), photon flux, X-ray source (synchrotron or anode) and energy, spot size, pass energy, dwell time, incident angle, substrate temperature, aperture size and distance, background gas, and fitting parameters such as background and peak shape. The general findings show that, on average, less than 50% of instrument parameters are recorded. A survey of X-ray sources revealed that over 50% of NAP-XPS experiments are conducted at synchrotrons. There is considerable variation in the frequency of parameter reporting: for instance, the analysis chamber pressure is reported 94% of the time, while dwell time is only reported 6% of the time. The large majority (92%) of papers contain fit data, but fewer than 50% of the literature report fitting parameters. Less than 5% of NAP-XPS studies are operando, among other findings. By emphasizing the critical role of various NAP and XPS parameters, we aim to promote best practices and enhance data reliability across the field.

SS-ThP-17 Landing Energy Dependent Surface Conformation of Electrosprayed Foldamer Molecules*, **Dennis Meier**[2],* Tufts University, Germany*; Shengming Zhang, Benedikt Schoof,* Technical University Munich, Germany*; Patrick Lawes,* Karlsruhe Institute of Technology (KIT), Germany*; Pengfei Zhao, Andreas Walz, Annette Huettig, Hartmut Schlichting, Joachim Reichert,* Technical University Munich, Germany*; Anthoula C. Papageorgiou,* Technical University Munich, Greece*; Ivan Huc,* Ludwig-Maximilians-University of Munich, Germany*; Johannes V. Barth,* Technical University Munich, Germany

Biomimetic molecules hold great potential for molecular devices, where preserving their secondary structure is crucial for maintaining functional properties. When assembled in well-ordered two-dimensional configurations, such molecules can exhibit unique characteristics. For example, helical aromatic foldamers are promising for molecular recognition and molecular machinery. Many of these macromolecules, however, cannot be sublimed by, e.g., organic molecular beam epitaxy onto surfaces in ultra-high vacuum (UHV). Electrospray controlled ion beam deposition (ES-CIBD) combines non-destructive landing onto surfaces with a low level of contaminants in UHV, due to soft ionization *via* electrospray ionization, mass filtering and control of the landing energy.

We addressed the deposition of two oligoamides of 8-amino-2-quinoline-carboxylic acid with different lengths on metallic surfaces in a UHV environment using ES-CIBD. In particular, we investigated how their landing energy during deposition influences the helical conformation. On the surface, the conformation of the molecules was unambiguously identified through real-space single-molecule imaging *via* scanning tunneling microscopy. At a low landing energy, the helix of the molecular structure was preserved after adsorption. Thermal treatment of the surface induces unfolding of the molecules. Increasing the landing energy resulted in mostly unfolded and partially folded molecules. At high surface coverages, a well-ordered self-assembly of the unfolded molecules was formed. We thus unravel the influence of the landing energy upon adsorption of complex molecules and provide a pathway for depositing intact molecules with well-defined secondary conformations on surfaces in UHV.

SS-ThP-18 Understanding Pt-Based Catalysts for Dehydrogenation of Methylcyclohexane for Use in Liquid Organic Hydrogen Carriers*, **Mengxiong Qiao**, Bhawana Rayamajhi, Andreas Heyden, Donna A. Chen,* University of South Carolina

Hydrogen is a promising source of clean and renewable energy, but a major challenge lies in its storage and transportation. The use of liquid organic hydrogen carriers (LOHC) allows hydrogen to be stored in organic molecules that are liquids at room temperature and therefore suitable for transportation through the existing infrastructure for petroleum. For example, the methylcyclohexane (MCH)-toluene pair has been used for the catalytic cycle of hydrogenation to store hydrogen and dehydrogenation to release hydrogen. While inexpensive and efficient catalysts are already available for hydrogenation, there is still the need for the development of selective dehydrogenation catalysts that inhibit deactivation due to carbon fouling.

In this work, model surfaces consisting of Pt(111), supported Pt clusters, and single-crystal Pt-Sn alloy surfaces were prepared in ultrahigh vacuum (UHV, $P \leq 2x10^{-10}$ Torr) and then transferred directly into a high-sensitivity flow reactor operated in recirculation mode for kinetic studies under realistic pressure conditions. The turnover frequency for MCH dehydrogenation on the Pt(111) surface was four times lower than for Pt clusters supported on highly oriented pyrolytic graphite (HOPG) at 300 °C, and this behavior is attributed to the higher activity of undercoordinated sites that exist on the clusters. Furthermore, the ordered Pt-Sn alloy surfaces prepared by depositing and annealing Sn films on Pt(111) had less carbon deposition compared to on Pt(111) itself, as determined by post-reaction X-ray photoelectron spectroscopy.

The reaction mechanism of MCHdehydrogenation to toluene was also investigated using a combination of DFT and microkinetic modeling techniques on Pt(111), Pt(100), and Pt(211). A microkinetic analysis with a continuous stirred tank reactor (CSTR) model identified the intrinsic catalytic activity, dominant reaction mechanism, and rate-controlling steps for the conversion of MCH to toluene. These results suggest that for Pt catalysts, the more open (100) and (211) facets are more active. However, the calculations also suggest that thermodynamically all Pt surfaces favor coke formation although the kinetic barriers for Pt(111) are at least 1 eV higher than for the more open surface facets.Thus, the most coke-resistant Pt surface should be the one in which the step sites are blocked, perhaps by an inactive metal like Sn.

SS-ThP-19 Structural Study of Rhodium-Based Metal Surfaces*, **Elizabeth Serna-Sanchez**, Alexis Gonzalez, Maxwell Gillum, Stephanie Danahey, Dan Killelea,* Loyola University Chicago

Heterogeneously catalyzed oxidation reactions, such as the catalytic process of converting CO to CO_2, are extensively utilized for the production of modern commodities. However, there is little information known about the atomic level details of these catalytic processes. In order to further our understanding of the process at an atomic level, the investigation herein will focus on characterizing structures of oxygen on Rh model catalysts. Scanning tunneling microscopy (STM) images illustrate how the behavior of oxygen is affected by features such as surface defects and step width. Alongside the STM, other techniques such as temperature programmed desorption (TPD), and low energy electron diffraction (LEED) are used to identify the various species of oxygen and the structures they form on the surface.

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SS-ThP-20 Self-assembly and On-surface Reactivity of β-diketonato Molecules on Au(111)*, **Chamath Siribaddana**, Nan Jiang,* University of Illinois Chicago

Self-assembly and on-surface reactions of organic molecular building blocks are two versatile processes that can be utilized to synthesize well-defined nanostructures with functional properties. It is essential to study the intricate details of these processes at the nanoscale to achieve their controllability. This would enhance the ability to create defect-free nanoarchitecture with long-range order and the desired symmetry. The final nanoarchitecture depends on the properties of the molecule/molecules used as the building block, i.e., symmetry, functional groups, and intermolecular interactions; properties of the substrate, i.e., crystallinity, symmetry, catalytic activity, and molecule-substrate interactions, and reaction conditions, i.e., substrate temperature and byproducts. Ultra-high vacuum (UHV) conditions and single-crystalline surfaces offer a pristine and controlled environment to synthesize nanostructures and investigate how these factors influence their formation. Scanning tunneling microscopy (STM), with its sub-molecular resolution, enables detailed probing of these factors at the local scale. In this study, the self-assembly and on-surface reactivity of a β-diketonato molecule on Au(111) were explored using UHV-STM across a range of substrate temperatures. At room temperature, the molecules self-assemble primarily through intermolecular halogen bonding, with minimal influence from molecule-substrate interactions. At higher substrate temperatures, an Ullmann coupling reaction via a surface-assisted activation of C-I leads to the growth of a robust self-assembly stabilized by intermolecular C-C bonds. The symmetry of the underlying substrate has a templating effect on the symmetry of this resultant robust covalent organic network type self-assembly despite not affecting its precursor assembly, which is conformationally flexible. The progression of the reaction with respect to the substrate temperature reveals thermodynamically favorable conditions for network units with varying sizes and symmetry. These insights into self-assembly and on-surface reactivity enhance the design of synthetic pathways that lead to nanomaterials with desired functionalities.

SS-ThP-21 Transformation of TiN to TiNO films via In-situ Temperature-dependent Oxygen Diffusion Process and their Electrochemical Behavior*, **Sheilah Cherono**, Dhananjay Kumar,* North Carolina A&T State University

Titanium oxynitride (TiNO) thin films represent a multifaceted material system applicable in diverse fields, including energy storage, solar cells, sensors, protective coatings, and electrocatalysis. This study reports the synthesis of TiNO thin films with controlled amount of oxygen using pulsed laser deposition. A comprehensive structural investigation was conducted by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Non-Rutherford backscattering spectrometry (N-RBS) and X-ray absorption spectroscopy (XAS), which facilitated a detailed analysis that determined the phase, composition, and crystallinity of the films. Structural control was achieved via temperature-dependent oxygen in-diffusion, nitrogen out-diffusion, and the nucleation growth process related to adatom mobility. The XPS analysis indicates that the TiNO films consist of heterogeneous mixtures of TiN, TiNO, and TiO_2 phases. The correlation between the structure and electrochemical behavior of the thin films was examined. The TiNO films with relatively higher N/O ratio, meaning less oxidized, were more electrochemically active than the films with lower N/O ratio (more oxidized films). Films with higher oxidation levels demonstrated enhanced crystallinity and greater stability under electrochemical polarization. These findings demonstrate the importance of substrate temperature control in tailoring the properties of TiNO film, which is a fundamental part of designing and optimizing an efficient electrode material.

This work was supported as part of the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at the North Carolina A&T State University under award DE-SC0023415. The work also used resources at the ALS of LBNL, supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH11231. Part of the work was performed using the resources of NSF-PREM Collaborative Research and Education in Advanced Materials Center (grant number DMR-2425119) and the Joint School of Nanoscience and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant ECCS-2025462). Also, the work was partially supported by project ELI-RO/RDI/2024-015 and National Nucleu Program LAPLAS VII – contract no. 30N/2023.

SS-ThP-22 XPS Study of Initial Oxygen Adsorption on ZrB2 (0001) at Room Temperature*, **Cosmic Gober**,* University of Illinois - Chicago

Zirconium diboride (ZrB_2) is an ultra-hard material with a melting point of 3246 °C, making it suitable for extreme environment applications such as hypersonic vehicles and cutting tools. Understanding its interactions with molecular oxygen (O_2) is crucial for predicting its performance. This study investigates the nascent stages of oxygen uptake on the ZrB_2(0001) surface at room temperature. A clean, well-ordered ZrB_2(0001) surface, confirmed by a characteristic (1x1) low energy electron diffraction (LEED) pattern, was exposed to O_2 dosages ranging from 0.01 to 1.0 L. X-ray photoelectron spectroscopy (XPS) was employed to track the evolution of surface composition. Analysis of the O 1s spectra following even minimal exposures reveals multiple distinct oxygen species. Two primary components were identified: one at a binding energy of 533.8 eV corresponding to oxygen adsorbed on the surface, and another at 531.4 eV attributed to oxygen incorporated into the subsurface region. These findings indicate that even at very low O_2 exposures at room temperature, oxygen not only dissociatively adsorbed onto the ZrB_2(0001) surface but also begins to penetrate the subsurface layers. This work demonstrates the capability of XPS to distinguish initial surface and subsurface oxygen species on ZrB_2(0001). The observation of subsurface oxygen at room-temperature exposures provides critical experimental data for understanding the onset of its oxidation pathway.

SS-ThP-23 Enhanced Electrocatalytic and Supercapacitance Performances of Transition Metal Oxynitride Thin Films*, **Brianna Barbee**,* North Carolina A&T State University

The importance of research in the field of non-conventional energy generation and storage cannot be overemphasized in order to be less dependent on limited resources in nature. Our research has established the effectiveness of the pulsed laser deposition (PLD) method for the synthesis of an emerging class of transition metal oxynitride (TMON) material systems in epitaxial thin film form. The material systems cover a wide range of compositions that exhibit the physicochemical properties needed in electrocatalysis and extended-life electrochemical energy storage. The attraction of TMONs over more widely studied transition metal oxides (TMOs) is rooted in the polarizability, electronegativity, and anion charge of nitrogen versus that of oxygen, which induces an enormous change in the physical and chemical properties of the resulting compounds. TMON films were deposited in the absence and presence of liquid nitrogen stage in the PLD chamber, which is capable of adsorbing the residual oxygen in the PLD chamber. The films were characterized using high resolution x-ray diffraction, x-ray reflectometry techniques, and x-ray photoelectron spectroscopy. The electrochemical supercapacitor measurements on the TiNO films using cyclic voltammetry have shown that the specific capacitance values are amongst the highest values reported for the recently top-tier nanoscale electrode materials.

SS-ThP-24 The Initial Oxidation Reactions of Compositionally Complex Alloys, (Cr-Mn-Fe-Co-Ni)*, **Farzad Bastani**,* University of Virginia, USA*; Keithen Orson, John R. Scully,* University of Virginia*; Petra Reinke,* University of Virginia, USA

The Cr-Mn-Fe-Co-Ni alloy with near-equimolar composition, known as the Cantor alloy, is a single-phase face-centered cubic solid solution and a compositionally complex alloy (CCA). These materials are stable as high configurational entropy solid solutions. CCAs can phase-separate into multi-phase systems and thus form compositionally and structurally complex surfaces. This complexity presents challenges for understanding surface reactions, particularly in catalysis and oxidation. This work examines the oxidation of polycrystalline Cantor, focusing on the composition and evolution of surface oxides as a function of time and temperature. Samples are sputter-annealed, and SRIM simulations model defect generation to consider near-surface defects in oxidation. Oxidation is studied under three conditions: (i) native oxide formed in ambient conditions, (ii) oxygen exposure in vacuum at variable temperatures, and (iii) cryogenic oxidation to “freeze” kinetics, suppress bulk diffusion, and isolate surface-limited reactions and O_2 dissociation. In-situ angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is used to track chemical composition and layering in the alloy and oxide. Ni oxide formation is consistently suppressed, and Cr and Mn preferentially form stable oxides under all conditions. Co oxide appears only in the native oxide, which also contains Cr hydroxide and Cr, Mn, and Fe oxides in proportions similar to those formed under vacuum oxidation, highlighting its role as a persistent surface state. Vacuum-grown oxides display temperature-dependent selectivity: at 77K, oxidation is limited and surface-bound; at 298K, Fe oxide is still observed; and at 600K, only Cr and Mn oxides persist, suggesting enhanced thermodynamic control and surface Fe depletion. Oxide structure varies by route: native oxides are chemically mixed and layered, while elevated temperature vacuum oxides form binary (Cr-Mn) phases.

These results show that surface oxide chemistry is governed more by kinetic and thermodynamic factors than by bulk composition. We also examine how surface enrichment and segregation (induced by identical treatments at different fixed temperatures) affect oxide structure and stability. Activation barriers are tracked by correlating temperature-dependent XPS data with selective oxide formation to map energy thresholds for surface composition changes. Future work will extend the materials space to multiphase alloys and explore the effects of crystallographic orientation, mechanical properties, and microstructural stability of Cantor alloys at cryogenic temperatures, including potential embrittlement, phase separation, and aqueous corrosion.

SS-ThP-25 Atomic-Scale Investigation of Electron-Induced Processes at Single-Atom Alloy Active Sites*, **Nima Rajabi**[1], Charles Sykes,* Tufts University*; Phillips Hutchison, Emily Carter,* Princeton University

Single-atom alloys (SAAs) have captured significant interest as promising thermo- and electro-catalytic materials and most recently in the plasmonic photocatalytic field due to their unique electronic and chemical properties. Unlike thermal catalysis, plasmon photocatalysis enables energy-efficient, selective molecular activation via localized surface plasmon resonance (LSPR), which reduces energy consumption and provides more control over the reaction. However, the details of the mechanism by which adsorbates react or desorb are still unclear. Using scanning tunneling microscopy (STM) and spectroscopy (STS), we investigate the topography and electronic structure of four different SAAs—NiAg(100), PtAg(100), PdAg(100), and RhAg(100)—and their role in electron-stimulated CO desorption. STS and density functional theory (DFT) allow us to correlate local density of states with electron energy and probe the mechanism of desorption. Specifically, we can identify states associated with transient negative ion (TNI) formation, which plays a crucial role in facilitating plasmon-induced charge transfer. In plasmon-driven photocatalysis, this TNI state can arise from chemical interface damping (CID) or Desorption Induced via Electronic Transition (DIET), key decay pathways of LSPR. Our results indicate that SAAs exhibit drastically different CO desorption rate dependence on electron energy.

Moving forward, we explored the possibility that the TNI state contributes to bond weakening, leading to more efficient CO removal—a major challenge in catalytic processes. To further support our experimental findings, we employed DFT calculations and embedded correlated wavefunction (ECW) methods. These studies provide additional insights into the electronic structure modifications induced by CO adsorption and desorption. DFT results align with experiments, showing similar desorption trends for RhAg, PtAg, and PdAg, while NiAg deviates, suggesting a different mechanism possibly linked to TNI state formation via electron injection. Our findings provide deeper insights into the electronic and catalytic properties of SAAs and offer guidance for designing more efficient and sustainable photocatalysts that minimize the use of precious metals.

SS-ThP-27 Oxygen Vacancies as a Reaction Switch for Cocatalysts-Free CO2 Photoreduction on CeO2/Mn3O4 Hybrid without Sacrificial Agent*, **Syed Bakhtiar**,* King Fahd University Petroleum and Minerals, Saudi Arabia

Photocatalysis offers an energy-efficient and renewable approach of CO_2 conversion into environmentally non-hazardous fuels and chemicals. However, the cutting-edge photo-catalysts mostly rely on sacrificial electron donors, and noble-metal cocatalysts hinder the progress of this field to real-world applications. Developing photo-catalysts that could work in the absence of sacrificial agents as well as noble-metal co-catalysts is highly desirable but remains challenging. As such, this work demonstrates a Z-scheme photo-catalyst having abundant oxygen vacancies in a flower-shaped CeO_2/Mn_3O_4 hybrid to facilitate the CO_2 photoreduction via exposure to visible-light. The CeO_2/Mn_3O_4 hybrid with oxygen vacancies promotes visible light absorption and charge carrier separation.The optimized $9CeO_2/Mn_3O_4$ yields 12 μmol h^{-1} of CO and 2.2 μmol h^{-1} of CH_4 without any noble metal catalysts or sacrificial reagents, which is ~13 times greater than that of standalone Mn_3O_4. In addition, the $9CeO_2/Mn_3O_4$ catalyst exhibits exceptional stability in photo-catalytic CO_2 reduction, with substantially zero drop-in activity during a 20-hour test period.The optimized photo-catalytic efficiency of $9CeO_2/Mn_3O_4$ is primarily due to its expanded range of light-absorption capacity and effective charge carrier retention, as demonstrated by UV-visible diffuse reflectance spectroscopy, PL analysis, transient photo-current spectra, and electro-chemical impedance spectroscopy. Therefore, this discovery has the potential to facilitate the fabrication of photo-catalysts for unsupported CO_2 reduction to biofuels and synthetic compounds.

Keywords: CeO_2/Mn_3O_4 hybrid, Flower morphology, Charge separation, Oxygen vacancy, CO_2 reduction.

SS-ThP-28 Mechanism of the Water-Gas Shift Reaction on Magnetite Catalysts Studied by Near-Ambient Pressure X-ray Photoelectron Spectroscopy*, **Akash Aoki**, Haruka Matsuda, Seikai Kurosawa, Yuki Tsujikawa, Hiroshi Kondoh, Tomoko K. Shimizu,* Keio University, Japan

The water–gas shift (WGS) reaction is a chemical process that produces hydrogen and carbon dioxide from water and carbon monoxide. It is widely used in industrial hydrogen and ammonia production, particularly in combination with steam methane reforming and the Haber–Bosch process. The WGS reaction proceeds in two stages: the high-temperature shift (HT-WGS), which primarily aims at hydrogen production, and the low-temperature shift (LT-WGS), which focuses on carbon monoxide conversion[1].

In this study, we address the unresolved mechanism of the HT-WGS reaction using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The commonly used Fe_2O_3-Cr_2O_3 catalyst is known to be reduced to Fe_3O_4 under reaction conditions. Therefore, we investigate the chemical states of both the catalyst surface, specifically $Fe_3O_4(111)$, and adsorbed gas species under reaction conditions.

A clean $Fe_3O_4(111)$ surface was prepared by the procedure reported previously[2]. H_2O and CO were co-exposed to the surface at a total pressure of 0.1 Torr with a 1:1 ratio, and XPS spectra were recorded during stepwise heating. Evolution of O1s and C1s spectra indicates increases of OH and H_2O, and formation of COOH. Fe2p and 3p regions confirms the oxidation and reduction states of $Fe_3O_4(111)$ during the chemical reaction.

These results not only provide clues for identifying the gas adsorption process in the HT-WGS, but also offer insights into the state of the Fe_3O_4 catalyst under reaction conditions. Moving forward, we aim to elucidate the reaction pathway of the HT-WGS through reproducibility tests under similar conditions and comparisons with results obtained under varying conditions.

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SS-ThP-29 Selective Hydrogenation of Styrene to Ethylbenzene Over a Pd/Cu(111) Single-Atom-Alloy Surface*, **Mohammad Rahat Hossain**, Michael Trenary,* University of Illinois - Chicago

The selective hydrogenation of styrene to ethylbenzene is of industrial significance due to its role in purifying xylene-rich streams used for para-xylene production, a key precursor to polyester fibers and PET plastics. Trace styrene can disrupt downstream separation and catalytic processes, especially in adsorptive purification systems. However, achieving high selectivity is challenging, as conventional catalysts often induce aromatic ring hydrogenation or xylene isomerization. Catalysts that can selectively hydrogenate the vinyl group while preserving the aromatic core are therefore essential. Single-atom alloy (SAA) catalysts have emerged as promising candidates for such transformations. In these systems, small amounts of an active metal are atomically dispersed in a less reactive host. The isolated active atoms serve as active hydrogen dissociation sites, while the surrounding relatively inert atoms suppress undesired over-hydrogenation. This ensemble effect enhances chemo-selectivity and reduces precious metal usage, making SAAs attractive platforms for probing structure–reactivity relationships in hydrogenation catalysis. In this study, we investigated the hydrogenation of styrene to ethylbenzene over a Pd/Cu(111) SAA under ambient pressure using reflection absorption infrared spectroscopy (RAIRS). The appearance of gas-phase ethylbenzene peaks below 3000 cm^{-1} (due to sp^3 C–H stretches) and the loss of the styrene vinyl bending mode at 909 cm^{-1} confirm successful hydrogenation.Auger electron spectroscopy (AES) of the post-reaction surface revealed carbon deposition, suggesting some dissociation. No spectral features associated with cyclohexyl ethylbenzene were detected, indicating high selectivity. The reaction showed 100% conversion with excellent selectivity toward ethylbenzene. A turnover frequency (TOF) of 36 s^{-1} at 380 K was observed, significantly higher than that for pure Cu, confirming the role of Pd sites.The activation energy was determined to be 31 ± 5 kJ/mol. The reaction order was found to be zeroth order in styrene

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[1] **JVST Highlighted Poster**

and first order in hydrogen. Further investigations on in-situ identification of surface-bound intermediates via RAIRS are currently in progress.

SS-ThP-31 Energetics of Methanol Adsorption on H- and CO-Precovered Pt (111) Surface*, **Arjan Saha**,* Washington State University*; Valeria Chesnyak,* Oregon State University*; Marcus Sharp,* Pacific Northwest National Laboratory*; Nida Janulaitis,* University of Washington*; Zbynek Novotny,* Pacific Northwest National Laboratory*; Charles T. Campbell,* University of Washington*; Líney Árnadóttir,* Oregon State University*; Zdenek Dohnálek,* Pacific Northwest National Laboratory

Understanding the adsorption energy of reactants on metal surfaces is fundamental to catalysis and electrocatalysis, including processes such as methanol synthesis, Fischer–Tropsch synthesis, and hydrogen fuel cells. These adsorption energies provide critical links between the catalyst structure and activity and serve as essential benchmarks for validating computational methods, such as density functional theory. Single crystal adsorption calorimetry (SCAC) is the only technique capable of directly measuring the heat of adsorption of molecules on single crystal surfaces [1]. While interactions between reactants and metal surfaces have been extensively studied, the influence of coadsorbed species such as hydrogen and carbon monoxide remains poorly understood. Here, we use SCAC to investigate how strongly bound adsorbates, such as H and CO, affect methanol adsorption and binding on Pt (111). We quantify the differential heat of adsorption of methanol on Pt (111) pre-covered with well-defined (1×1) H and ($\sqrt{3} \times \sqrt{3}$) R30° CO adlayers [2]. The initial heat of adsorption decreases from 65 kJ/mol on bare Pt (111) to ~55 kJ/mol on H/Pt (111) and to ~45 kJ/mol on CO/Pt (111). The coverage-dependent heats further reveal details about the changes in methanol-surface and methanol-methanol interactions. These results demonstrate the significant impact of coadsorbed species on methanol binding and provide important insights into surface interactions relevant to electrodes and catalytic metal nanoparticles.

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SS-ThP-32 Correlating Stress Development and Nanopattern Formation of Si Under Low-Energy Ion Bombardment*, **Marlene Ludwig**, Ellie Stonecipher, Benli Jiang, Karl Ludwig,* Boston University

Self-organized pattern formation on materials as a result of broad-beam Ion Beam Sputtering (IBS) has long been observed but important disagreements about fundamental causes remain. Previous research has confirmed the presence of surface nanopatterns on Si under room-temperature IBS and shown that the surface of the crystalline sample is amorphized. It's also known that codeposited impurities on samples during bombardment potentially affect sample surface stress. To minimize impurities, our experiments focused on bombardment using an experimental arrangement of demonstrated purity which was checked by X-ray Photoelectron Spectroscopy (XPS). This allows results to be attributed to IBS itself, rather than as a result of codepositing impurities. Silicon thin wafers were bombarded with 500 eV Ar^+ ions at a 65° incidence angle, which is known to be the regime in which self-organized patterns form. Both real-time and *post-facto* methods were used to analyze samples. During bombardment, the Multi-Beam Optical Stress Sensor (MOSS) method was used to study wafer curvature and determine stress development in real-time. After bombardment, *post-facto* Atomic Force Microscopy (AFM) and Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) were used to analyze surface morphology and determine possible patterning. While stress development was observed, optimization of experimental conditions is still ongoing and aims to elucidate the relationship between stress development and nanopattern formation.

This work was partly supported by NSF DMR-2117509, NSF REU-2244795, and MRI-2216008.

SS-ThP-33 XPS Analysis of PTFE Decomposition Induced by 10–500 eV Electron Beam Irradiation*, **Hao Yu**, Jackson King, Sylwia Ptasińska,* University of Notre Dame

Per- and polyfluoroalkyl substances (PFAS) have become a significant environmental concern due to their exceptional resistance to degradation in aquatic environments, leading to increasingly stringent global regulations on their production, use, and recycling. Among PFAS treatment strategies, electron beam irradiation has attracted attention for its ability to degrade highly stable fluorinated compounds. Low-energy electron (LEE, below 30 eV) irradiation, as a precise and controllable method for inducing specific chemical modifications on surfaces, may also provide a pathway for initiating bond scission and surface functionalization through its interaction with PFAS.

Polytetrafluoroethylene (PTFE; C_2F_{2n+2}) was selected as the research target due to its simple PFAS structure and exceptional chemical stability among PFAS compounds. PTFE films with a thickness of 12 µm were deposited onto carbon tape, which was then mounted on a stainless steel holder. An electron gun installed in the X-ray photoelectron spectroscopy (XPS) system, normally used to neutralize surface charge accumulation, was employed as the LEE irradiation source. The electron energy range was 10–500 eV, with a beam current of 100 µA, for durations of up to 24 hours under vacuum. In-situ XPS measurements were performed before and after LEE irradiation, under a base pressure of approximately 2×10^{-10} mbar. Survey spectra from the range of 1200 to 0 eV, and core-level spectra of C 1s, O 1s, and F 1s were recorded.

Electron energies in the 10–500 eV range were found to induce chemical changes in the PTFE surface. Survey spectra showed a general decrease in signal intensity with irradiation, accompanied by modification in both C 1s and F 1s regions. At higher energies, fluorocarbon environments were rapidly altered, while lower-energy electrons produced more gradual but still detectable changes. The lowest-energy regime (10 eV) showed significant consistency with the dissociative electron attachment (DEA) process. These findings highlight the energy-dependent pathway for electron-driven PTFE degradation and provide insights relevant to controlled polymer surface modification.

SS-ThP-34 Quartz Crystal Microbalance Measurement of Premelting at the Ice-Substrate Interface*, **Blake R Hance**, Steven Sibener,* University of Chicago

Premelting of ice, the formation of a quasi-liquid water layer at the surface of ice below the bulk melting point, is poorly understood but instrumental in understanding interactions at the ice surface. We present a study of premelting using a novel quartz crystal microbalance (QCM) method to acoustically probe the quasi-liquid layer (QLL) at the buried ice-substrate interface at a variety surfaces. The quasi-liquid layer is found to vary from slightly thicker than the thickness of one ice bilayer (0.37 nm) at -15 C to 2.25 nm at -0.5 C. We find that hydrophobiciy has a strong impact on the temperature dependence of premelting, with the QLL being thicker on more hydrophobic surfaces at lower temperature. These findings improve our understanding of the impact of substrate features on ice premelting at buried interfaces and demonstrate the utility of QCM for investigating these systems.

SS-ThP-35 Visualizing Inhomogeneous Molecular Adsorption Structures on a Solid Surface by Three-Dimensional Atomic Force Microscopy*, **Keisuke Miyazawa**, Takeshi Fukuma,* Kanazawa University, Japan

In three-dimensional atomic force microscopy (3D-AFM), AFM tip is three-dimensionally scanned at a solid-liquid interface, and interaction force applied to the tip is recorded to generate a 3D force image with subnanometer-scale (< 1 nm) resolution. Recent studies suggested that 3D-AFM images show molecular adsorption structures at various solid-liquid interfaces in real space. This unique capability of 3D-AFM is strongly demanded in many industrial fields, where molecular adsorption layer is widely used for controlling surface properties. For example, magnetic hard disks (HDs) in hard disk drive (HDD) are coated with a 1-2 nm lubricant layer made of perfluoropolyether (PFPE) to protect the HD from mechanical damage. To improve the reliability and capacity of HDD, understanding of the real-space molecular adsorption structures of lubricants is required for further thinning of the lubricant layer; however, it is difficult because of the lack of a direct imaging technique. In this study, we demonstrated 3D-AFM measurements of PFPE lubricant layers on the HD (Fig. 1a). Figure. 1b shows the xz cross-section obtained from the 3D force image (Fig. 1c) measured on a commercially available HD. The molecular-scale fibrillar contrasts in Fig. 2b-c directly show the complicated and inhomogeneous arrangements of PFPE lubricant molecules. We also performed systematic experiments using different thicknesses and molecular species of PFPE lubricants and successfully visualized the changes in the molecular adsorption structures using 3D-AFM. As shown in this research, 3D-AFM provides molecular adsorption structures in real space and contributes to further molecular-scale improvement of practical materials in various industrial fields.

SS-ThP-36 Reorientation in Vertically Aligned Polycrystalline Mos2 Films Due to Shear*, Shima Karimi,* North Carolina A&T State University

MoS_2 films grown via chemical vapor deposition are found in a growing number of applications. The size and orientation of the film depends on the growth kinetics set by the deposition parameters. Growth along the edges is energetically favored relative to highly passivated basal plane which leads to vertical alignment. While this vertical orientation is common, it leaves reactive sites exposed, making the films more sensitive to oxidation and humidity. In this work, molecular dynamics simulations were carried out to investigate the reorientation of vertically aligned MoS_2 films during contact and shear. An Indent–Hold–Slide–Retract (IHSR) procedure was applied to model adhesion and frictional behavior. We observe that bonding between the exposed edges of the opposing surfaces drives pull-out of individual MoS_2 sheets from the surface. These flakes are then entrained into the sliding interface and are reoriented horizontally during subsequent sliding which results in lowered friction. The transition toward basal alignment produces a marked reduction in friction and resembles the experimentally observed “run-in” process of MoS_2 coatings. This effect is more pronounced in films with larger grain sizes. We hypothesis that the disorder present in smaller grain sized films produces a higher degree of initial passivation which in turn reduces sheet pull out and reorientation. These results provide atomistic insight into how grain size, density, and microstructural order govern the early sliding response of MoS_2 coatings, linking edge bonding, adhesion, and basal-plane reorientation to the emergence of stable low friction.

SS-ThP-37 Transition Metal Carbides as Pluripotent Catalysts and Support: Materials Synthesis and Reaction Studies*, Keithen Orson, Fanyue Kong, Antonio Valavanis, Prasanna Balachandran, Kory Burns, Ji Ma, Chris Paolucci, Leonid Zhigilei, Sen Zhang,* ***Petra Reinke,*** University of Virginia

A long standing challenge in heterogeneous catalysis is the reliance on Pt-group metals which play a major role in the energy transition to renewables. They have been designated by DOE as critical elements and finding substitutions remains a daunting challenge. Transition metal carbides such as Mo and W carbides can be used as catalysts, supports and electrodes but present with complexity in surface chemistry and materials synthesis. The reactions on TMCs as a compound catalyst require therefore modified scaling laws and reassessment of reaction mechanisms in conjunction with materials characteristics.

We combine methods for materials synthesis far from equilibrium, computational approaches to describe carbide surface reactions, and surface and electrochemical studies of reactions and material stability. For the carbide materials we aim to control carbide composition, doping with transition metals, defect inventory, and carbide phase for modulation of electronic and surface structure.[2] To reach the unique combination of carbide material characteristics and produce carbide phases not accessible with conventional thermal synthesis, we employ additive manufacturing (AM) using laser powder bed fusion (LPBF) and pulsed laser ablation in liquids (PLAL). Defects, phase distribution and surface reactions are studied with STEM, XPS and related methods. We include DFT calculations to understand and predict the role of defects and phase. We will discuss our results in AM based synthesis and control of carbide materials and introduce carbide surface recovery using graphite inclusions studied with ambient pressure XPS. An initial set of DFT calculations links materials characteristics to surface chemistry, and a workflow to develop potentials for MD calculations will be presented. This presentation illustrates our integrated approach which includes computational and experimental studies on carbide surface reactions including electrochemical characterization, materials synthesis using AM, and the concomitant development of potentials for MD simulations. We will discuss results from all aspects of our work and show their integration in pursuit of carbide development.

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SS-ThP-39 On-Surface Synthesis of Porous Nanographene with Spin-½ and Spin-3/2 States*, Mamun Sarker,* University of Nebraska - Lincoln*; Haiyue Huang,* University of California, Los Angeles*; Percy Zahl,* Brookhaven National Laboratory*; Prineha Narang,* University of California, Los Angeles*; Alexander Sinitskii,* University of Nebraska - Lincoln

Molecular design is a powerful tool for growing graphene nanostructures with atomic precision, enabling control over their electronic and physical properties. Precisely tuning these properties is essential for advancing the next generation of graphene-based electronic and spintronic devices. Porous nanographene with tailored spin systems represents a new frontier for carbon-based quantum and spintronic materials. Its intrinsic pore architecture, combined with unpaired π-electrons, provides a unique platform to stabilize and control spin states. Here, we demonstrate the on-surface synthesis of porous nanographene from a carefully designed molecular precursor using a combination of solution-phase chemistry and on-surface cyclodehydrogenation under ultra-high vacuum (UHV) on Au(111), as visualized by scanning tunneling microscopy (STM). Scanning tunneling spectroscopy (STS) revealed clear magnetic fingerprints, including a weak Kondo resonance. Depending on precursor design, the system hosts either spin-½ or spin-3/2 ground states. By combining differential conductance spectra and orbital maps with density functional theory (DFT) and advanced multiconfigurational CASSCF calculations, we confirmed their spin states. This work establishes porous nanographene as a versatile platform for engineering multi-spin systems, advancing prospects in molecular magnetism, spintronics, and quantum science.

Surface Science
Room 209 CDE W - Session SS-FrM

Surface Science of Reduced Dimensional Materials

Moderators: Moritz Eder, TU Wien, **Naihao Chiang**, University of Houston

8:15am **SS-FrM-1 On-Surface Synthesis of Planar/Nonplanar Porous Graphene Nanoribbons and Nanosheets*, Junfa Zhu,*** University of Science and Technology of China **INVITED**

The low-dimensional porous graphene nanomaterials might have intriguing electronic properties and open exciting possibilities in the field of functional materials. By using rationally designed precursor molecules, on-surface synthesis (OSS) approach has emerged as a powerful platform for the synthesis of porous low-dimensional graphene-based nanostructures with atomic precision. In this presentation, we report our recent works on the synthesis of planar/nonplanar porous graphene nanoribbons and nanosheets on different metal surfaces. We have successfully synthesized the one-dimensional planar graphene nanoribbons (GNRs) containing periodic [14]annulene pores on Ag(111) and the two-dimensional non-planar graphene nanosheets containing periodic [30]annulene pores on Au(111), originating from a same precursor [1]. Two distinct reaction pathways on the two surfaces were regulated by different thermodynamic and kinetic mechanisms. In addition, a novel nonplanar porous [32]annulene graphene nanosheet that contains the narrowest periodic nanopores up to date was also successfully synthesized by the dissymmetrical debromination and regioselective coupling reactions of precursor molecules on an Au(111) surface [2]. With the combination of the scanning tunneling microscopy (STM), synchrotron radiation photoemission spectroscopy (SRPES) and density functional theory (DFT) calculations, we identified the reaction products, intermediates precisely, and obtained insights into the reaction mechanism. Moreover, the electronic properties of these porous graphene nanoribbons were also precisely characterized.

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8:45am **SS-FrM-3 Deuterium Adsorption on N-Doped Carbon Materials*, Buddhika Alupothe Gedara,*** *Mi Yeon Byun, Zdenek Dohnalek, Zbynek Novotny, Tom Autrey,* Pacific Northwest National Laboratory

Nitrogen-doped carbon materials have been identified as promising candidates for hydrogen activation and storage, however, there is little experimental insight into the nature of the hydrogen interaction in response to the changes in the physical behavior of these materials. In this study, we investigated deuterium adsorption on N-doped highly oriented pyrolytic graphite (N-HOPG) and porous, layered N-doped carbon (NC) materials using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy. N-dopants were introduced to HOPG through low-energy N_2+ irradiation, while NC was obtained by pyrolysis of glucose and graphitic carbon nitride (g-C_3N_4). Nitrogen is embedded in the carbon materials in two predominant configurations: as graphitic N (N substituted in the hexagonal C lattice) and pyridinic N (substitutional N adjacent to a C vacancy). In both N-doped carbon materials the amount of graphitic N exceeds the amount of pyridinic N, at 6.9 and 4.2 atomic percent (at.%), and 4.3 and 2.7 at.%, in in N-HOPG and NC respectively. Atomic deuterium (D) was generated by D_2 cracking over a hot tungsten (W) filament. XPS data showed that upon D exposure at 220 K, the pyridinic N peak (398.0 eV) shifted to a higher binding energy by +1.2 eV for HOPG and +1.1 eV for NC, while the graphitic N peak (400.7 eV) remained unchanged, indicating that the D atoms bound solely to pyridinic N. All the pyridinic N on HOPG could be saturated with D atoms, whereas only approximately 30% of the pyridinic N could bind D atoms in NC. This is attributed to the porosity of NC, which prevents atomic D from reaching some pyridinic N located within the pores. Deuterium fully desorbed from HOPG at 773 K, while complete desorption from NC was observed above 873 K. This study demonstrates a strong correlation between D adsorption on freestanding graphene and layered porous carbon materials, providing a comparative analysis of the N-doping effects on the surfaces and interfaces of carbon materials in both idealized planar model systems (N-HOPG) and high surface area materials such as NC. The authors gratefully acknowledge the support of U.S. Department of Energy, Office of Science, Basic Energy Sciences, Physical Behavior of Materials under Award No. 80110.

9:00am **SS-FrM-4 Ion Beam-induced MoS_2 Surface Modification: An XPS Study of Ar+ and Ar Gas Cluster Ion Beam Treatments*, Francesco Laudani,*** *Markus Sauer, Dmitry Polyushkin,* Technische Universität Wien, Austria*; Lorenzo Pettorosso,* Technische Universität Vienna, Austria*; Jakob Rath, Jakob Hemetsberger, Annette Foelske,* Technische Universität Wien, Austria

Two-dimensional (2D) materials are a class of crystals structured as sub-nanometer sheets with no dangling bonds on the basal plane. Molybdenum Disulfide MoS_2 is the second most studied 2D material after graphene [1]. The material's electrical and chemical properties can be tuned by creating defects. The most studied type of defect due to its ease of formation is the sulfur vacancy, usually found to be a p-dopant [2] and to increase of chemical reactivity of the surface as the defect presents increased chemical reactivity [3]. One way of creating such vacancies is ion beam exposure. It provides a precise and spatially resolved possibility of creating defects on the material's surface due to preferential sputtering of sulfur [4]. XPS studies of ion beam exposure effects on MoS2 have previously been featured in several publications which showed molybdenum (IV) to reduce to an oxidation state whose nature is not yet precisely defined [5,6,7]. As the nature of the treated surface is still not fully understood our study aims to gain further understanding through a more in-depth investigation of ion beam treatment. We compare freshly cleaved surfaces of MoS_2 crystals (molybdenite) and CVD-deposited MoS_2 monolayers using Ar^+ ion beam at 500 eV and 1 keV to induce preferential sputtering of sulfur and follow the evolution of molybdenum's chemical environment by recording the Mo 3d region using XPS. In addition, we investigate the effects of Gas Cluster Ion Beams with clusters Ar^+_{2500} at 20 keV energy and Ar^+_{1000} at 2.5 keV energy, respectively, to understand how a different energy transfer may affect the surface transformation for monomer compared to gas cluster ion beams [8]. The surface properties are then investigated further by monitoring the reactivity by exposing the sample to ambient conditions and following the re-oxidation process in air. The results allow for a better understanding of the surface modifications and a preliminary model for the effects of Ar ions on MoS_2 is proposed which might contribute to a more precise tailoring of MoS_2 (electronic) properties in the future.

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9:15am **SS-FrM-5 Model Studies of the Surface Structure and Stability of Metal Nanoparticles on Oxide Surfaces Under Catalytic Conditions*, Ravi Ranjan,*** *Francisco Zaera,* University of California - Riverside

The surface structure and properties of copper (Cu) and platinum (Pt) nanoparticles (NPs) supported on tantalum oxide films ($Cu/TaO_x/Ta$ and $Pt/TaO_x/Ta$) have been investigated under ultrahigh vacuum (UHV) and high-pressure conditions using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD), together with carbon monoxide (CO) as a probe molecule. After oxidizing the surface of the tantalum disc in situ under UHV, both metals were vapor-deposited onto tantalum at room temperature, and the resulting surface sites were titrated with CO at 77 K for the Cu-deposited surface and 300 K for the Pt-deposited surface. Sequential growth of Cu led to the formation of distinct adsorption sites, including atoms at the metal–oxide interface and on (100) and (111) facets. These Cu NPs remained stable under UHV up to at least 500 K. However, under atmospheric CO pressures, they exhibited reduced thermal stability, remaining intact only between 300 and 450 K. Furthermore, CO adsorption was found to be significantly more exothermic under UHV conditions compared to ambient CO environments, indicating a notable pressure dependence in adsorption energetics.

In contrast, Pt deposition at room temperature resulted in a less dramatic development, manifested by a slight shift in the a-top CO adsorption frequency, the only feature observed in the RAIRS data, to higher wavenumbers with increasing deposition time. No bridging CO features were detected, suggesting the formation of relatively small and isolated NPs. Pt NPs were observed to diffuse into the subsurface upon heating above around 600 K, suggesting limited thermal stability on the TaOx support. These studies provide insights into the structural evolution and dynamic behavior of metal NPs on oxide supports under conditions relevant to catalysis.

9:30am **SS-FrM-6 Exploring the Catalytic Potential of Supported MgO Nanostructures for CH_4 Conversion*, Arephin Islam*[1]**, Brookhaven National Laboratory*; Jose Rodriguez,* Brookhaven National Laboratory and State University of New York at Stony Brook

Natural gas, primarily composed of methane, is a versatile energy vector with significant potential for efficient energy utilization. Converting methane into valuable hydrocarbons, such as ethane and ethylene, at low temperatures without deactivation challenges remains a critical objective. MgO nanostructures have emerged as promising candidates for methane activation due to their unique surface properties, while Cu-based catalysts demonstrate potential for selective methane oxidation at reduced temperatures. This study examines the growth and reactivity of MgO nanostructures on Cu_2O/Cu(111) and Au(111) substrate using scanning tunneling microscopy (STM) and synchrotron-based ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). Mg deposition onto the "29" structured copper oxide film promotes oxygen transfer from the Cu_2O/Cu(111) substrate to Mg, forming MgO and CuO_x phases. The resulting structures exhibit diverse morphologies, including embedded MgO nanostructures (1–3 Mg atoms) and randomly dispersed MgO nanoparticles. AP-XPS and STM analyses reveal that MgO nanostructures (0.2–0.5 nm wide, 0.4–0.6 Å high) embedded in Cu_2O/Cu(111) substrates activate methane at room temperature, dissociating it primarily into CH_x (x = 2 or 3) and H adatoms with minimal C adatom formation. At 500 K, these structures facilitate C–C coupling into ethane and ethylene with negligible carbon deposition and no catalyst deactivation, significantly outperforming bulk MgO catalysts, which require temperatures exceeding 700 K. Density functional theory (DFT) calculations support these experimental findings, showing that methane activation is a downhill process on MgO/Cu_2O/Cu(111) surfaces. Methane dissociation is driven by electron transfer from copper to MgO and the presence of under-coordinated Mg and O atoms. The formation of O–CH_3 and O–H bonds lowers the energy barrier for C–H bond cleavage in methane. Furthermore, DFT studies indicate that smaller Mg_2O_2 clusters exhibit stronger binding and lower activation barriers for C–H dissociation, while larger Mg_3O_3 clusters enhance C–C coupling due to weaker *CH_3 binding. To understand the role of Cu, MgO was also deposited on inert Au(111) surface followed by similar XPS and STM experiments. These results highlight the critical role of size in optimizing the catalytic performance of MgO nanostructures for selective methane conversion.

9:45am **SS-FrM-7 Automated Matter Manipulation to Create Artificial Lattice Structures*, Ganesh Narasimha*[2]***, Mykola Telychko, Wooin Yang, Arthur Baddorf, An-Ping Li, Rama Vasudevan,* Oak Ridge National Laboratory

The precise arrangement of matter using scanning tunneling microscopy (STM) presents a controlled route for engineering structures that exhibits designer quantum states. Nonetheless, the sensitive nature of STM tip poses significant operational challenges in assembling diverse lattice geometries with tailored functionalities. In this work, we introduce a reinforcement learning (RL) driven experimental framework to construct artificial nanostructures via spatial manipulation carbon monoxide (CO) molecules on a copper substrate. The pipeline integrates deep learning-based image analysis for molecule recognition that is coupled with an RL agent that predicts optimized parameters for molecule manipulation. Initial manipulation strategies are generated through stochastic sampling of tip parameters—bias voltage, current setpoint, and tip speed—which are compiled into action sequences serving as training data for the RL agent. Upon training, the agent is deployed on the STM for construction of artificial structures. The workflow uses additional techniques such as data augmentation, active drift correction, and high-precision controls, thereby facilitating the creation of artificial lattice structures.Acknowledgement:Research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Scientific User Facilities Division as part of the QIS Infrastructure Project, “Precision Atomic Assembly for Quantum Information Science” and performed at the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

(Acknowledgement: This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Scientific User Facilities Division as part of the QIS Infrastructure Project, “Precision Atomic Assembly for Quantum Information Science” and performed at the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory).

10:00am **SS-FrM-8 Morton Traum Student Award Announcement***,*

10:30am **SS-FrM-10 Atomic-Scale Exploration of Low-Dimensional Materials*, Nathan Guisinger,*** Argonne National Laboratory, USA **INVITED**

Low-dimensional materials functioning at the nanoscale are a critical component for a variety of current and future technologies. From the optimization of light harvesting solar technologies to novel electronic and magnetic device architectures, key physical phenomena are occurring at the nanometer and atomic length-scales and predominately at interfaces. This talk will cover research and review capabilities within the Center for Nanoscale Materials (CNM) at Argonne National Laboratory, which is one of the five Department of Energy Nanoscale Research Centers. In this presentation, I will discuss low-dimensional material research occurring in the Nanoscale Synthesis and Characterization (NSC) Group at the (CNM). I will discuss the synthesis and characterization of advanced material platforms, such as graphene and borophene, and a more recent focus on artificial lattices. Specifically, the synthesis of artificial graphene nanoribbons by positioning carbon monoxide molecules on a copper surface to confine its surface state electrons into artificial atoms positioned to emulate the low-energy electronic structure of graphene derivatives. We demonstrate that the dimensionality of artificial graphene can be reduced to one dimension with proper “edge” passivation, with the emergence of an effectively gapped one-dimensional nanoribbon structure. Remarkably, these one-dimensional structures show evidence of topological effects analogous to graphene nanoribbons. Guided by first-principles calculations, we spatially explore robust, zero-dimensional topological states by altering the topological invariants of quasi-one-dimensional artificial graphene nanostructures. The robustness and flexibility of our platform allows us to toggle the topological invariants between trivial and non-trivial on the same nanostructure. Our atomic synthesis gives access to nanoribbon geometries beyond the current reach of synthetic chemistry and thus provides an ideal platform for the design and study of novel topological and quantum states of matter.

11:00am **SS-FrM-12 Using Two-Dimensional Covalent Organic Frameworks to Stabilize Single-Atom Catalysts on Model Surfaces*, Yufei Bai,*** Indiana University Bloomington*; David Wisman,* NAVSEA Crane*; Steven Tait,* Indiana University Bloomington

Single-atom catalysts (SACs) combine the advantages of homogeneous and heterogeneous catalysts by limiting the reaction sites to isolated single metal atoms with well-defined chemical properties. A metal-ligand coordination method to stabilize SACs has been previously developed by our group, in which 1,10-phenanthroline-5,6-dione (PDO) was used as the ligand to coordinate with metals such as Pt, Fe, and Cr to form stable metal single sites on the gold surface.[1] To further enhance the metal loading per unit surface area while preserving catalyst stability, we explored utilizing the uniform pores of single-layered two-dimensional covalent organic frameworks (2D COFs) for the stabilization of these SACs. Highly stable on-surface 2D COFs with well-defined pore sizes were synthesized on model surfaces under ultra-high vacuum (UHV) or ambient conditions, subsequently serving as templates to host ligand-coordinated Pt SACs. Under UHV conditions, the formation of 2D COF with hexagonal symmetry on the Au(111) surface was achieved by surface-mediated Ullmann-type radical coupling of COF precursor 1,3,5-tris-(4-bromophenyl)benzene (TBB).[2] Subsequent deposition of PDO and Pt on the COF surface allowed the formation of single-site Pt catalysts via coordination interaction. Surface characterization, including scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), demonstrated the confinement of PDO in the COF pores and the existence of oxidized Pt, indicating its single-atom nature. Under ambient conditions, an imine-linked 2D COF was formed on the highly oriented pyrolytic graphite (HOPG) surface via a solid-vapor interface mechanism, resulting in a high-quality network with long-range order.[3] Subsequently, PDO and PDO-coordinated Pt were deposited onto

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

the COF surface, and their surface distribution and interactions with the COF network at the liquid/solid interface were characterized by STM. Those results were compared to the self-assembly behavior of PDO and PDO-coordinated Pt complexes on graphite without 2D COF. STM analysis provides insights into the intermolecular interactions that determine the supramolecular structure and patterning on the surface. In both systems studied, the 2D COF has a significant impact on the distribution of Pt-PDO complexes. These systems which combine COF confinement and metal-ligand coordination strategy to stabilize SACs offer the possibility to achieve higher stability and greater metal loading.

References

(1) *J. Chem. Phys.* **2015**, *142*, 101913.

(2) *Chem. Commun.* **2009**, 4456-4458.

(3) *J. Am. Chem. Soc.* **2013**, *135*, 10470-10474.

11:15am **SS-FrM-13 Probing the Promotion or Inhibition of TiO_2 Atomic Layer Deposition on Si(111) Surfaces Modified by Basic Amines***, **Tyler Parke**, Andrew Teplyakov,* University of Delaware

The use of small molecule inhibitors (SMI) in area selective atomic layer deposition (AS-ALD) processes has gained widespread attention for their capability to confer selectivity onto ALD substrates with near-atomic scale resolution. In TiO_2 AS-ALD processes using hydrogen-terminated silicon (H-Si) and oxidized silicon (HO-Si), some nitrogen-containing compounds have been shown to selectively block titanium precursors from the H-Si non-growth surface and prevent selectivity loss.

In this study, an array of basic amines, such as aniline, parafluoroaniline (pFA), pyridine, and trifluoroethylamine (TFEA) were investigated for their use as inhibitors or promoters of TiO_2 thermal ALD processes on the (111) single-crystal surface of H-Si and HO-Si. While some compounds act as a small molecule inhibitor (SMI) on these surfaces during the TiO_2 ALD processes, blocking precursor adsorption, some, such as para-fluoroaniline (pFA), act as a promoter of TiO_2 deposition, enhancing growth rate well beyond what is expected for the unmodified HO-Si growth surface.

Nucleation patterns during the first few cycles of ALD on amine-modified silicon surfaces were probed by atomic force microscopy (AFM) to determine the cause of inhibition or promotion. To further understand these patterns, surface topography was compared between surfaces reacted with basic amines -in vapor-phase and in solution. The bonding of the amines to each surface was confirmed with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR), which were correlated with density functional theory (DFT) simulations to model the resulting surface structures. Understanding the amine-modified surface structures and what drives them to promote or inhibit ALD processes will allow for a greater capability to tune surface selectivity, and thus a wider scope of 3D architectures to be formed and integrated into nanoelectronic devices.

11:30am **SS-FrM-14 Oxides Formed on Multi-Phase Complex Concentrated Alloys: Nanoscale Spectroscopic Imaging with XPEEM and Tof-SIMS***, **Keithen Orson**, Samuel Inman,* University of Virginia*; Jerzy Sadowski,* Brookhaven National Laboratory*; Derk Rading, Julia Zakel,* ION-TOF USA, Inc.*; John Scully, Petra Reinke,* University of Virginia

Complex concentrated alloys (CCAs) present an opportunity to design new alloys with tunable mechanical and corrosion properties. The inclusion of second phases for strengthening is desirable, but second phases can be detrimental to localized corrosion resistance even if both phases individually have good corrosion resistance. The chemistry and structure of the corrosion-protectant passive layer is not well understood for these complex alloys. The air-formed native oxide of a two-phase CCA with the composition $Al_{0.3}Cr_{0.5}Fe_2Mn_{0.25}Mo_{0.15}Ni_{1.5}Ti_{0.3}$ is characterized with X-ray photoemission electron microscopy (XPEEM) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). These hyperspectral imaging techniques combine nanoscale spatial resolution with spectroscopic information and produce $>10^6$ spectra. There are sharp differences in oxide character between the FCC and $L2_1$ phases of this nominally two-phase alloy. Clustering analysis of the XPEEM and ToF-SIMS images reveals that there are at least two additional phases present in the alloy which are identified by their distinct oxide contributions: nanoscale Ti-rich and Al-rich inclusions that comprise <1% of the total alloy, making them difficult to study without these techniques. Minor inclusions may nevertheless have large implications for local breakdown of corrosion resistance. XPEEM and complementary X-ray photoelectron spectroscopy (XPS) show that the primary elements in the passive film are Al, Cr, Fe, and Ti. Mo is present in the 4+,5+, and 6+ oxidation states, acting as an aliovalent cation. Spectral features observed in Cr spectra with XPEEM indicate that the Cr chemical environment varies between the passive film formed on the FCC matrix and the L21 second phase, and the minor inclusions have distinct passive films than the surrounding alloy. To further understand what oxide species form in the passive film, a controlled oxidation of the clean alloy surface was done in UHV conditions and combined with XPEEM and XPS to understand what oxides form during early oxidation. This controlled oxidation reveals that Cr, Al, and Ti oxidize in the first few monolayers of Oxygen exposure. Mo, Fe, and Mn oxidize to a smaller degree, and Ni does not contribute at all during the first 100 Langmuir of oxygen exposure. The composition and rate of oxide formation also varies based on the underlying phase. Direct observations of the passive film over the different phases provide insight into the local corrosion resistance CCAs at phase boundaries, aiding in the future design of corrosion resistant multi-phase CCAs.

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