Surface Science Division
Room On Demand - Session SS-Contributed On Demand
Surface Science Contributed On Demand Session

SS-Contributed On Demand-1 Development of Low Thermal Budget Si Epitaxy and High-K/Metal Gate Stack for Atomically Precise Electronic Devices*, **Evan M. Anderson**, D. Campbell, J. Ivie, S. Schmucker, P. Lu, X. Gao, L. Tracy, R. Arghavani, E. Bussmann, A. Baczewski, T. Lu, D. Ward, S. Misra,* Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) uses a scanning tunneling microscope to create donor devices in an atomically thin layer doped beyond the solid solubility limit, enabling unique device physics. This presents an opportunity to investigate digital electronics at the atomic limit. APAM has been excellent for producing one-off devices for physics experiments, but many materials challenges must be resolved before integration with industry standard metal-oxide-semiconductor (MOS) technology. A functional device, such as a transistor, additionally requires epitaxial Si to cap and activate the dopants and a gate on the surface to control it. Low thermal budget (LT) processes are needed to limit dopant diffusion to preserve atomic precision, though this introduces defects in the materials and interfaces.

The parameter space for optimizing LT epitaxy is large and material characterization is difficult, making the path forward unclear. Transmission electron microscopy (TEM) indicates the LT epitaxy yields minimal structural defects, while secondary ion mass spectrometry (SIMS) reveals impurities. However, the subtle variations within these observations do not reliably correlate with Hall measurements of the donor layer, making the importance of these defects ambiguous. To resolve this, we have separately developed an LT high-k/metal gate stack to produce MOS capacitors to study the defects in the APAM donor layer, epitaxial Si, and Si/oxide interface. The gate stack is of sufficient quality that C-V characteristics are dominated by the underlying LT epitaxial layers. C-V measurements of MOS capacitors consisting of LT epitaxial Si and the APAM donor layer provide densities of electrically active defects introduced by LT epitaxy that can be correlated to TEM and SIMS. This combination of tools allows thorough understanding of the impact of LT epitaxy parameters on device performance, enabling optimization the LT epitaxial Si for integration of industry compatible MOS technology with APAM devices for atomically precise digital electronics.

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SS-Contributed On Demand-4 Mechanisms of Electrocatalytic Reduction of N_2 at Vanadium and Cobalt Oxynitride Surfaces: Impacts of Metal Oxophilicity and Π-Backbonding*, **Adaeze Osonkie**, A. Ganesan, P. Chukwunenye, F. Anwar, I. Rashed, F. D'Souza, T. Cundari, J. Kelber,* University of North Texas

The electrochemical nitrogen reduction reaction (NRR) is an environmentally and energy-friendly alternative to the Haber-Bosch process for the production of NH_3, which currently accounts for 2% of the world's energy usage. While earth-abundant catalysts, especially transition metal oxides and oxynitrides, have received intense recent scrutiny, there is little fundamental understanding of basic reaction mechanisms at the electrolyte/surface interface; including the roles of N-metal vs. O-metal interactions, or of metal-N_2 interactions. We present here a comparison between oxophilic vanadium oxides/oxynitrides and cobalt oxynitride. Vanadium is more oxophilic, while Co ions exhibit higher d-orbital occupancy. Herein, electrochemical, absorption spectroscopy, and XPS measurements, supported by DFT calculations for vanadium oxide and oxynitride films, are compared to those for cobalt oxynitride films. All films were formed by magnetron sputter deposition. Electrochemical and absorption spectroscopy data demonstrate (a) N_2 reduction in vanadium oxides and oxynitrides occurs primarily at O-supported V centers; and (b) NRR activity for cobalt oxynitrides indicates ~ one order of magnitude increase in activity relative to the vanadium systems, as well as evidence of high selectivity for NRR vs. the hydrogen evolution reaction (HER) under identical conditions. DFT calculations indicate that both N_2 absorption and reduction at O-supported vanadium sites (V_O) is energetically favored over N-supported (V_N) centers, but that this difference in energies should decrease sharply for less oxophilic systems, such as Co. Initial calculations also suggest that the order-of-magnitude enhanced NRR activity and selectivity for the cobalt oxynitride film is due to increased 3d-orbital occupancy vs. the vanadium systems, resulting in enhanced π-backbonding and more facile protonation of adsorbed N_2.Implications of these results for future studies and the design of Earth-abundant NRR-selective catalysts will be discussed.

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SS-Contributed On Demand-7 Advanced Thermoporometry Characterization of Disordered Mesoporous Materials*, **Henry R. N. B. Enninful**, D. Schneider, R. Kohns, D. Enke, R. Valiullin,* Leipzig University, Germany

Elaborate determination of the pore structure of mesoporous solids offers important guidance towards optimal design of various applications such as catalysis, molecular separations and adsorption, among others. Routinely used characterization tools, such as gas sorption, typically utilize the general adsorption isotherm (GAI) equation derived for ordered pore systems. Te complex morphology of disordered porous solids, with its resulting cooperativity effects in thermodynamic phase transitions, renders characterization more complex than what the GAI provides.

In this work, we present a recently developed serially connected pore model (SCPM), which extends the by incorporating cooperativity effects in phase transitions arising from pore complexity. Modeled as statistically disordered linear chain of pores, the SCPM will be validated with data from phase transitions in a synthesized porous silica material of similar pore construct, MCM-41. As an analogue to gas sorption (adsorption/desorption) studies, solid-liquid phase transitions (freezing/melting) of water in porous materials will be employed to correlate with the theoretical model and to reveal geometric disorder in SBA-15 material.

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SS-Contributed On Demand-10 Electrical Resistance Response of a Zno Single-Crystalline Substrate to Trace Ethanol Under Pulsed Air Jet Irradiation*, **Taku Suzuki**, Y. Adachi, T. Ohgaki, I. Sakaguchi,* National Institute for Materials Science, Japan*; M. Nakamura, H. Ohashi, A. Aimi, K. Fujimoto,* Tokyo University of Science, Japan

The pulsed jet technique was applied to measure the electrical resistance response of a Zn-terminated ZnO(0001) substrate to trace ethanol in the air to simulate the realistic working surface of a semiconductor gas sensor in a vacuum. The resistance response to the trace ethanol under the static atmospheric pressure air was well reproduced by the periodic pulsed jet technique with the optimal irradiation conditions, in which the pressure in the vicinity of the surface transiently reached 2 kPa. The behavior of the resistance upon the pulsed jet irradiation was discussed in terms of the ionsorption of oxygen. Because the background pressure was kept low enough during the pulsed jet irradiation, the reaction products during the ethanol sensing, such as acetaldehyde, has been successfully detected at the elevated temperature above 400 K by temperature programmed desorption-mass spectrometry (TPD-MS).

SS-Contributed On Demand-13 Elucidate 3D Structure of PM2.5 Aerosol Particles using ToF-SIMS*, **Zihua Zhu**, Y. Zhou,* Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99354, USA*; F. Mei,* Atmospheric Science and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, 99354, USA

The primary and secondary particles are the main sources compose of the atmospheric aerosols. Primary emissions, such as biogenic emission, biomass burning, and vehicle exhausts, not only provide primary particles to the atmosphere but also supply precursors for the formation of secondary aerosol (SA). Many analysis tools have been used to study chemical components of SA, elucidating that SA is made up of complex components. However, most of the analysis tools only analyze the aerosol bulk properties, lack of capabilities to provide necessary information to elucidate the particles' two-dimensional (2D) and three-dimensional (3D) structure. Such information is critical in many aerosol models, because it can be used to distinguish homogeneous and heterogeneous reactions. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool with several unique advantages. For example, it can provide elemental, isotopic and molecular information simultaneously. Also, its information depth is very shallow (typically 1-3 nm), and surface-specific information can be collected. In addition, it has excellent sensitivity (ppm level) and an excellent spatial resolution (sub-micron). In this research, we used ToF-SIMS to study PM2.5 SA particles collected in a typical Beijing winter pollution case in 2019. Combined with traditional scanning electron microscope and bulk analysis data, the 3D structure of aerosol particles under different pollution conditions was determined. Our results provide critical information to improve current aerosol formation models.

SS-Contributed On Demand-16 Facet-Dependent Study of the Interaction of Water Vapor With Fe_2O_3 at Near Ambient Conditions*, **Nabajit Lahiri**, D. Song, M. Zong, X. Huang, X. Zhang,* Pacific Northwest National Laboratory*; K. Stoerzinger, P. Adiga, Q. Carvalho,* Oregon State University*; M. Blum,* Lawrence Berkeley National Laboratory*; K. Rosso,* Pacific Northwest National Laboratory

Hydroxylation and wetting of iron oxide surfaces are one of the most ubiquitous processes occurring in nature as well as in technological systems. However, probing such a phenomenon in-situ under ambient conditions tend to be extremely challenging. Here, we present our recent developments using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) in conjunction with density functional theory (DFT) calculations, to probe the facet-dependent interaction of molecular water vapor on hematite nanoparticles. Size- and morphology-controlled synthesis were conducted to generate hematite nanocrystals with specific facets exposed, namely, (001), (012), and (104). The physisorption of molecular water and subsequent formation of hydroxyl species on the surface of hematite was then monitored in-situ using the O 1s photoelectron spectra acquired over a range of water vapor pressures (10^{-9} Torr < $p(H_2O)$ < 0.1 Torr). The results clearly reveal that the exposed crystallographic facet has a dramatic impact on the hydroxylation and wettability of the hematite surface.Although the onset of hydroxylation for the three surfaces occur at similar relative humidity values of about 10^{-7} Torr, the (104) facet was seen to undergo significantly higher net surface hydroxylation when compared to the (012) and (001) facets. The present study greatly advances our knowledge of the interaction of water with hematite and paves the way for the rational design of better photocatalysts for solar water splitting applications. Furthermore, such studies are essential for gaining deeper insight into various natural processes including, iron-mediated mobility of inorganic and organic pollutants in soil, nitrogen fixation, and corrosion, to name a few.

SS-Contributed On Demand-19 Influence of Geometric Disorder on Fluid Phase Transitions in Disordered Mesoporous Solids*, **Henry R. N. B. Enninful**, D. Schneider, D. Enke, R. Valiullin,* Leipzig University, Germany

Majority of porous solids used in industrial processes such as energy storage, separations and catalysis possess structural disorder over varying length scales. These disorder effects strongly affect the properties of the confining fluids in the pores. Hence, detailed quantification of structural disorder with correlation to fluid phase behavior is a necessary step towards optimization for practical applications.

Employing the serially connected pore model, (SCPM), we have determined the impact of a number of disorder-related parameters, including effect of pore chain length, "powder effect" and inter-connectivity effect on phase transitions in disordered mesopore spaces. Additionally, we have showed experimental results from solid-liquid phase transitions obtained by NMR cryoporometry and gas-liquid transitions observed from nitrogen sorption experiments to corroborate the theoretical predictions from the SCPM.

We conclude that, the SCPM has the potential of explaining many features of experimentally observed phase transitions in disordered mesoporous solids.

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SS-Contributed On Demand-22 Use of Ultra Thin Atomic Layer Deposited Capping Layers to Increase Stability in Thermally Processed Metalcone Thin Films*, **Vamseedhara Vemuri**, N. Strandwitz,* Lehigh University

Molecular layer deposition (MLD) and atomic layer deposition (ALD) are sequential, self limiting thin film deposition techniques, used to fabricate organic, inorganic, and inorganic-organic hybrid thin films. The hybrid organic-inorganic films deposited using MLD are usually metal alkoxides that are also termed as metalcones. Metalcone films can be subjected to thermal processing to selectively remove the organic parts of the film and induce porosity. However the as deposited and thermally processed metalcone films are unstable in ambient atmosphere due to the moisture absorption and permeation, which alters the chemical properties of these films. Since the dielectric constant of the water is very high (70-80), the net dielectric constant of these films increases after moisture absorption thus affecting the electrical properties. To preserve the chemical stability and electrical properties of metalcones, this work examines the use of an ultra thin ALD film grown over the as deposited and thermally processed films.

We report the growth of alucone thin films using trimethylaluminum and ethylene glycol as precursors for MLD and water (H_2O) as an oxygen source for ALD reactions. The as deposited MLD films are subjected to thermal processing from 150-350˚C in inert atmosphere and under UV light to remove the organic components and induce porosity. We examined the thermally induced changes in film's chemistry, thickness, density, etch rate and dielectric constant.

Incorporation of the organic components, formation of M-O-C bonding and water absorption is confirmed using FTIR in the as deposited MLD films. By subjecting MLD films to thermal processing the decrease in intensity of hydrocarbon bonds and changes in thickness, density compared to pure MLD films can be observed by FTIR and x-ray reflectivity respectively. The dielectric constant of these films is measured using capacitance-voltage measurements. The dielectric constant of the thermally processed films with a thin ALD layer decreases compared to only thermally processed films indicating that the thin ALD layer thus preserves electrical properties of the film. The as deposited and thermally processed films with and without the ultrathin ALD layer are subjected to CF_4/O_2 plasma etch and the MLD films without an ALD layer shows more than double the etch rate compared to the MLD films with an ALD layer. Both the decreased dielectric contant and etch rates show that the ALD layer acts as a barrier to prevent moisture absorption and preserve the chemical stability and electrical properties of the film.

SS-Contributed On Demand-25 In-Situ Visualization of Surface Plasmon-Driven Hot Carrier Generation With Photoconductive AFM*, **Hyunhwa Lee,** K. Song,* Institute for Basic Science (IBS), Korea (Republic of)*; M. Lee,* Inha University, Korea (Republic of)*; J. Park,* Institute for Basic Science (IBS), Korea (Republic of)

Understanding the inter-coupling between surface plasmon and the electronic distribution in metallic nanostructures is a challenging topic to develop applications of plasmonic solar-cells and efficient photodetectors. Non-radiative surface plasmon decay produces highly energetic electron-hole pairs on the metal surface with desirable characteristics.[1] Since these carriers, called hot electron/or hot hole, dissipate their energies within the femtosecond resolution, it is hard to directly observe the fast-delivering during photocatalytic reaction. Thus, research on identifying surface plasmon-driven hot carrier dynamics at the nanoscale is of great importance. Here, we demonstrate the direct observation of surface plasmon-driven hot carriers created in a Schottky platform using photoconductive atomic force microscopy (pc-AFM).[2-3] We fabricated Au nanoprism on n-type TiO_2 film and p-type GaN substrate for detection surface plasmon-driven hot electron and hot holes, respectively. We show significant enhancement of photocurrent in the plasmonic platforms under light irradiation, providing direct evidence of plasmonic hot carrier generation. Experimental and numerical analysis verified that a confined |E|-field surrounding a single Au nanoprism spurred resonant coupling between localized surface plasmon resonance (LSPR) and surface charges, thus boosting hot carrier generation. Furthermore, geometrical and size dependence on the extraction of LSPR-driven hot carriers suggests an optimized pathway for their efficient utilization. The direct visualization of hot carrier flow at the nanoscale provides significant opportunities for harnessing the underlying nature and potential of plasmonic hot carriers.

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SS-Contributed On Demand-28 Impact of Hot Hole Transport on Photocatalytic Activity in Au Nanoprisms/p-Gan under Water Splitting Reaction*, **Kyoungjae Song,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee,* Institute for Basic Science (IBS), Korea (Republic of)*; M. Lee,* Inha university, Korea (Republic of)*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Under the irradiation of light, excited carriers with high kinetic energy (1-3 eV) can be generated in plasmonic metals. The carriers consist of hot electrons and hot holes. The hot holes have a considerable potential due to their more energetic kinetics relative to hot electrons. To utilize hot holes by localized surface plasmon resonance, a plasmonic metal/ p-type semiconductor Schottky platform was proposed. Utilizing Au nanoparticle/ p-GaN photocathode, hot holes can be detected and photocatalytic reaction by hot holes can also be measured.

To investigate the correlation between photocatalytic activity and hot holes by surface plasmon, we fabricated size-controlled Au nanoprisms/ p-GaN photocathode using an e-beam evaporator. The electrical properties of the platform were measured by the conductive atomic force microscopy and Kelvin probe force microscopy. The triangle-shaped Au has a thickness of 10 nm and a length of 90 nm, 140 nm, and 220 nm. The small-sized Au nanoprism exhibited a high external quantum efficiency by a factor of 2 compared to that of the large one. We found that the amount of hydrogen and oxygen gas evolution increased as the size of Au nanoprism decreased from 220 nm to 90 nm. The results indicate the enhanced hot hole flux by amplification of localized surface plasmon resonance leads to the promotion of hydrogen and oxygen gas evolution reaction.

SS-Contributed On Demand-31 Observation of Atomic-scale Gliding Effect on Hydrophilic Surfaces at High Humidity*, **Tae Won Go,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee, J. Kim,* Institute for Basic Science (IBS), Korea (Republic of)*; D. Lee, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Most semiconductors in modern industries consist of hydrophilic surfaces, which play a crucial role in the performance of nano-electromechanical systems (NEMS). The nanoscale friction behavior of adsorbed water layers on hydrophilic surfaces includingsilica and mica with exfoliated graphene was investigated by friction force microscopy (FFM) in various relative humidity (RH) conditions. Depending on the RH, the change in the topography and friction of surfaces could be observed. The friction on both of mica and silica initially increased with respect to RH and started to decrease at an intermediate RH (~ 70%). At high RH (> 98%), the height of graphene and silica were non-distinguishable, and graphene showed higher friction than silica. In addition, the water intercalation between graphene and hydrophilic surfaces formed subdomain structure within graphene sheet, which showed enhanced friction due to more efficient energy dissipation mediated by electron-phonon interaction. These results suggest that the abundance of adsorbed water molecules at probe/hydrophilic surface interface lead to atomic-scale gliding that overcomes capillary and viscosity effects. The finding may provide useful insights for semiconductor applications in ambient conditions.

SS-Contributed On Demand-34 Pt/Ag/TiO_2 Plasmonic Nanodiode for Extraction of Surface Plasmon-Driven Chemicurrent*, **Mincheol Kang,** B. Jeon, Y. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; H. Lee,* Institute for Basic Science (IBS) , Korea (Republic of)*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Solar energy conversion to improve catalytic performance is actively studied, and the design of photocatalysis incorporating surface plasmon is drawing significant attention as a highly competitive catalyst system. Important factors of surface plasmon are size, shape, and material of plasmonic metal nanostructures, which affect plasmonic excitation, absorbance, and hot electron collection.In this study, we fabricated Schottky nanodiodes with nanoscale Pt/Ag patterns with controlled size and shape using nanosphere lithography and reactive ion etching. Plasmonic nanodiodes composed of Pt/Ag/TiO_2 were used to detect exothermic surface reaction-induced hot electrons under hydrogen oxidation. In this system, the surface temperature was measured using the thermovision to distinguish contributions of the plasmonic effect and the photothermal heating effect. When the light of the particular wavelength region (400~500 nm) is incident on the diodes, both chemicurrent and catalytic activity of hydrogen oxidation were amplified by the plasmonic effect of antenna Ag. In addition, we show the visualization of the plasmonic effect using the finite difference time domain simulations. The novel scheme of antenna-reactor using plamonic nanodiodes may offer a strategy for advanced hot-electron-based catalytic and photovoltaic devices.

SS-Contributed On Demand-37 Disruption of Small Alcohol Intermolecular Interactions at Defect Sites on Au(111)*, E. Maxwell, L. Garber, J. Baker, C. Rogers, H. Kaleem, **Ashleigh Baber,*** James Madison University

Gold-based catalysts have received great study as supports and nanoparticles for heterogeneous catalysis in recent years, in part due to the ability of Au to catalyze reactions at low temperatures in oxidative environments. Surface defects are known as active sites for low temperature chemistry on Au surfaces, so a full understanding of the interplay between intermolecular interactions and surface morphology is essential to an advanced understanding of catalytic behavior and efficiency. In a systematic study to better understand the adsorption and intermolecular behavior of small alcohols (C_1-C_4) on Au(111) defect sites, coverage studies of methanol, ethanol, 1-propanol, 1-butanol, and 2-butanol have been conducted on Au(111) using ultrahigh vacuum temperature-programmed desorption (TPD). These alcohols molecularly adsorb on the Au(111) surface, and high resolution experiments reveal distinct terrace, step edge, and kink adsorption features for each molecule. The hydrogen-bonded (H-bonded) networks of these small alcohols on Au(111), except 1-butanol, have been previously imaged on the molecular level at low temperatures by ultrahigh vacuum scanning tunneling microscopy (UHV-STM). Primary alcohols up to 1-propanol exhibit planar H-bonded zigzag chain networks while 2-butanol arranges in tetramer clusters of H-bonded molecules due to steric hindrance inhibiting the proximity of molecules on Au(111). Interestingly, the adsorption, desorption, and molecular structure of 1-butanol on Au(111) has yet to be investigated. In this study, the desorption energy of small primary alcohols was shown to trend linearly with increasing carbon chain length through the range of C_1-C_4, indicating that the H-bonded molecular packing of 1-butanol resembles that of methanol, ethanol, and 1-propanol. The distinction between the desorption of 1- and 2- butanol highlights the role of intermolecular interactions due to the difference in molecular packing structures on Au(111). Furthermore, by studying the energetics of terrace H-bonded networks in comparison with molecular adsorption to undercoordinated step edge and kink defect sites, it is shown that the contribution of stabilizing intermolecular interactions and van der Waals (vdW) forces to the overall adsorption energy is less for small alcohols adsorbed at kink sites and similar for those adsorbed at step edge sites relative to alcohols adsorbed on the Au terrace.

SS-Contributed On Demand-40 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers*, K. P. S. Boyd, E. Cook, M. Paszkowiak,* ***Erin Iski,*** The University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an external applied potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Additional studies examining the role that surface temperature played in the formation of the adatom islands will also be discussed. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

SS-Contributed On Demand-43 Resonant ARPES Reveals the Origin of the 2DEG in SrTiO$_3$ and SriTiO$_3$ Heterostructure*,* ***Jessica McChesney****, X. Yan, H. Hong, D. Fong,* Argonne National Laboratory

The origin of the two dimensional electron gas/liquid (2DEG) at the surface of bare SrTiO$_3$ and SrTiO$_3$-based heterostructures has been under debate since it was first observed in SrTiO$_3$/LaAlO$_3$. This debate is largely fueled by the ubiquity of the 2DEG from often seemingly contradictory conditions. For instance, the 2DEG has been both observed and not observed for freshly cleaved SrTiO3, or in-vacuum annealed SrTiO$_3$ wafers, argon-sputtered surfaces, and for various heterostructures where a minimum overlayer thickness is required. Using resonant angle-resolved photoemission spectroscopy, we show that it is not oxygen defects that are the requirement for the formation of the 2DEG but instead any non-interacting electron donor, including those produced as part of the photoemission process that can induce sufficient band bending for forming the quantum well 2DEG.

SS-Contributed On Demand-46 Self-selective Formation of Organized 1D and 2D GaBi Structures on Crystal-phase Modulated GaAs Nanowires*,* ***Yi Liu****, R. Timm, S. Benter,* Lund University, Sweden*; E. Young,* University of California at Santa Barbara*; S. Lehmann, K. Dick,* Lund University, Sweden*; C. Palmstrøm,* University of California at Santa Barbara*; A. Mikkelsen,* Lund University, Sweden

Yi Liu[1], Sandra Benter [1] , Elliot Young[2], Sebastian Lehmann[1], Kimberly A. Dick[3], Chris J. Palmstrøm[2], Anders Mikkelsen[1], and Rainer Timm[1]

[1] Department of Physics and NanoLund, Lund University, P.O. Box 118, 221 00 Lund, Sweden

[2] Materials Department and Dept. of Electrical and Computer Engineering, University of California - Santa Barbara, CA 93106, USA

[3] Centre for Analysis and Synthesis and NanoLund, Lund University, P.O. Box 124, 221 00 Lund, Sweden

Semiconductor devices made up of only a few atoms in size with precise positions have been highly challenging but are crucial for new applications in quantum computing and sensing. III-V semiconductor nanowires (NWs) have the merit of controllable axial stacking of different crystal phases with exposing different crystal facets, which is ideal for studying surface functionalization at the nano scale. Bismuth (Bi) incorporation and alloying in III-V semiconductors such as InAsBi and GaAsBi have become popular due to a number of promising properties, such as predicted band inversion and topological behavior in the case of high Bi concentrations. However, the realization of alloys with high Bi content by epitaxial growth has remained challenging, and GaBi bonds have been considered to be unstable.

We use the sidewall facets of NWs with both zinc blende (Zb) and wurtzite (Wz) segments as templates, and study self-selective growth under Bi deposition by low-temperature scanning tunneling microscopy and spectroscopy (STM/S). We observe the site-selective Bi incorporation on the surface via the Bi-for-As exchange reaction. More specifically, we find a crystal structure dependent surface alloying process, where ordered GaBi structures such as 2D islands and 1D atomic chains of a few atoms are formed on Wz {11-20} facets, while randomly distributed single Bi sites are found on Zb {110} facets. This self-selective formation process of ordered GaBi nanostructures is attributed to different diffusion barriers and surface geometries of the different surface facets. Lastly, signs of a length-dependent energy confinement effect in Bi-chains are observed via STS, which also indicates a smaller band gap on the surface of GaBi islands made up of a few tens of atoms on GaAs NWs. X-ray photoelectron spectroscopy with nanoscale beam size has also been used to evaluate chemical states before and after Bi incorporation.

Our results indicate a promising way to realize versatile high precision design of device structures with controllably positioning of materials at the atomic scale, by utilizing tailored NW heterostructure and surface facet variations.

SS-Contributed On Demand-49 Growth and Morphology of Well-ordered Metal Doped-CeO$_x$(111) Interfaces*, L. Du, E. Ginting,* ***Jing Zhou****,* Department of Chemistry, University of Wyoming

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity [1]. Doping ceria with additional metal elements can enhance its thermal stability. The interaction of metal dopants with ceria can also lower the activation energy needed for the release of oxygen, which can result in the improvement of its redox properties and oxygen storage capacity and consequently the enhancement of its catalytic activity. To understand the chemistry of doped-ceria mixed oxides, it is of crucial importance to determine their surface structures at the fundamental level. We present our study on the growth of ceria thin films with Ti and Mn dopants and the understanding of their structures using X-ray photoelectron spectroscopy, low-energy electron diffraction, as well as scanning tunneling microscopy under ultrahigh vacuum conditions. In our study, well-ordered CeO$_x$(111) (1.5 $<x<2$) thin films with controlled degree of Ce reduction and atomic structures were grown on a Ru(0001) single crystal substrate [2]. Metal-doped ceria mixed oxide interfaces were prepared by depositing Ti or Mn over CeO$_x$(111) thin films. Co-deposition of Ce with metal dopants during the film growth can produce well-ordered Ce$_{1-y}$M$_y$O$_x$(111) (M=Ti, Mn) mixed oxide films [3]. Our data show that dopant types and growth conditions can influence the surface structures, electronic and redox properties of ceria. Effects of Mn and Ti dopants in ceria were further investigated for supported Ni. Compared to pure ceria, addition of metal dopants in ceria can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as small metal nanoparticles upon heating. The chemical state of Ni is dependent on the nature of the ceria support. Modified structures and electronic properties of ceria by dopants provide promotional effects in the activity and stability of Ni nanoparticles in the dry reforming of methane reaction. The research is sponsored by the National Science Foundation Grant (Award Number: CHE1151846) and Wyoming Carbon Engineering Initiative from School of Energy Resources at University of Wyoming.

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SS-Contributed On Demand-52 STM and XPS Studies of Co Nanoparticles on Reducible CeO$_2$(111) Thin Films*,* ***Jing Zhou****, L. Du,* University of Wyoming

STM and XPS Studies of Co Nanoparticles on Reducible CeO$_2$(111) Thin Films

Linze Du and Jing Zhou*

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Cobalt metal catalysts have been of great interest as economical and promising catalysts for ethanol reforming and dry reforming of methane reactions. Ceria can be a suitable choice as the catalytic support for Co since unique redox properties and oxygen storage capacities of ceria can influence the size, structure, chemical state, and thus the catalytic performance of Co. To elucidate the nature of the reactivity, it is of significance to gain a fundamental understanding of the structure and electronic properties of Co particles on ceria supports. Here we report our studies of Co deposited on fully oxidized CeO_2(111) and reduced CeO_x(111) thin films using scanning tunneling microscopy and X-ray photoelectron spectroscopy. Ceria thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. The growth of Co particles was investigated as a function of Co coverages, deposition temperatures, post-deposition annealing temperatures, as well as degrees of Ce reduction. At 300 K, oxidation of Co to Co^{2+} occurs on fully oxidized CeO_2. At low Co coverages (<0.2 ML), Co^{2+} is the predominant species. With the increase of the Co coverage, both metallic and Co^{2+} species can be present on CeO_2. Metallic Co is the major species formed on partially reduced ceria. Co forms two-dimensional small particles on ceria at room temperature. With further heating to 1000 K, the particles can agglomerate into three-dimensional structures. However, they are on average less than 1 nm high at 1000 K. A comparison of the growth of Co on CeO_2(111) with our previous studies of Au, Ni, Pt, and Rh at the same coverage demonstrates that Co forms the smallest clusters, which suggests a stronger Co-ceria interaction. Our study presents model Co-ceria catalytic systems for further investigation of the chemistry in the reforming process related with particle sizes, chemical states and support effects. The research was sponsored by the National Science Foundation Career Grant (Award Number: CHE1151846) and Wyoming Carbon Engineering Initiative from School of Energy Resources at University of Wyoming.

SS-Contributed On Demand-55 Electronic Structure of a Carbon Dot Monolayer on TiO_2(110)*, **Jan Eric Beckord**, M. Hengsberger,* University of Zurich, Switzerland*; A. Cannizzo,* University of Bern, Switzerland*; J. Osterwalder,* University of Zurich, Switzerland

Carbon dots are nanometer-sized particles with a carbon core and a functionalized organic shell. Our research focuses on their photocatalytic properties: for example, the oxygen evolution reaction at titanium dioxide surfaces under visible light irradiation is significantly improved [1]. To elucidate the electronic structure and dynamics of this system, we adsorbed a single layer of carbon dots with an average size of 4 nm on a clean rutile TiO_2(110) surface from aqueous solution under vacuum. Our XPS measurements revealed a coverage of approximately one monolayer, an increased upward band bending of the n-doped substrate and a lowered work function. A continuum of additional occupied and unoccupied states is found using ultraviolet photoemission spectroscopy (UPS) and two-photon photoemission spectroscopy (2PPE) due to the various molecular orbitals on the carbon dots. The analysis of 2PPE measurements at different photon energies does not reveal any resonant transitions which would result in an increased intensity. Optical absorption and fluorescence measurements of the carbon dots in aqueous solution support this claim, as the typical broad absorption and excitation-dependent fluorescence of carbon dots with such an electronic structure are observed [2]. These continua of electronic states facilitate exciton generation from visible light, explaining the function of carbon dots as effective photosensitizers. The excited electrons are then efficiently transported to the substrate, as the band alignment forms a p-n-junction at the interface. We show this with time-resolved 2PPE, where the observed transfer time according to our interpretation is in the femtosecond range, much faster than the relaxation time of 6 ns previously measured with time-resolved fluorescence spectrometry in aqueous solution [3]. We conclude that carbon dots donate excited electrons to the substrate, leaving catalytically active holes behind. Additionally, we found excellent long-term stability even in ambient air and under strong light, making this system suitable for applications under ambient conditions.

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SS-Contributed On Demand-58 UHV Growth and Characterization of Ga_2O_3 on Cu_2O (111)*, **Mert Taskin**, T. Kälin, C. Hanisch, J. Osterwalder,* University of Zurich, Switzerland

Photoelectrochemical cells have been attracted more and more attention in recent years because they are promising candidates to store clean and renewable solar energy in chemical form. Cu_2O, a natural p-type semiconductor with a direct bandgap of 2.17 eV, has a conventional conduction band position slightly above the water reduction potential and offers a low-cost photocathode for unassisted water splitting devices [1]. However, bare Cu_2O lacks photovoltage under illumination. Overlayers of n-type Ga_2O_3 can be employed to reduce the interfacial recombination effects due to the adequate conduction band alignment with Cu_2O, leading to an increase in photovoltage [2]. In this work we investigate the electronic properties and the morphology of surfaces and interfaces of UHV-grown Ga_2O_3 on Cu_2O(111) with surface science methodology. In particular, we study the effect of post-annealing treatments and the influence of a reconstruction of the Cu_2O(111) substrate prior to Ga_2O_3 deposition.

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SS-Contributed On Demand-61 Tracking the Ultrafast Dynamics of Surface Photoinduced Reactions on Amorphous Surfaces With With Time, Mass, and Energy Resolution*, **Mihai Vaida**,* University of Central Florida

In surface-aligned-reactions (SAR), reagent species produced by the photolysis of aligned molecules adsorbed on crystalline solids tend to move in well-defined directions relative to the crystal surface. In this case, the degrees of freedom of surface chemical reactions are restricted, and therefore the reaction outcome is in general predictable. In contrast to SAR, on amorphous surfaces, molecules can have various adsorption geometries and therefore their reaction outcome is unforeseeable. In this work, to understand the effect of random molecular adsorption geometries on the surface reaction, the ultrafast photoinduced reaction dynamics of the deuterated methyl iodide (CD_3I) molecules adsorbed on amorphous cerium oxide films is investigated. An experimental technique that combines surface mass spectrometry with femtosecond pump excitation-dissociation followed by probe ionization-detection in employed. This technique can be used to decipher the complex surface reaction dynamics through detection of reaction intermediates and final products with time-, mass-, and energy resolution. A minimum dissociation time of 126 fs is measured after the A-band excitation of the CD_3I molecules. The faster gas-phase release of CD_3 relative to I, indicates that the CD_3I molecules are predominantly connected to the surface through the iodine atom. After the dissociation, the fragments are not produced at a steady rate, decaying as a function of the pump-probe time delay, which indicates a further surface reaction. The decay time of I (8 ± 0.5 ps) is similar to the release time of I_2(8.5 ± 0.3 ps), while the decay time of CD_3 (2.5 ± 0.3 ps) is similar to the release time of the CD_3I (2.2 ± 0.3 ps) molecules that are reformed on the surface. Interestingly, no I_2 or CD_3I molecules are detected within the first 800 fs after the initial excitation. This is due to the high kinetic energy with which the fragments are released after dissociation. This energy is lost through collisions with the surface or neighboring adsorbates to facilitate the bimolecular reaction, as reveled by monitoring the time-of-flight of the mass peaks as a function of the pump-probe time delay.

SS-Contributed On Demand-64 Investigating the Effect of Sn Vapor Deposition Parameters on Nb-Sn-O Coordination on a Highly-Ordered Oxidized Nb(100) Substrate*, **Sarah Willson**, R. Farber, S. Sibener,* University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but is limited to operating temperatures of ~ 2 K. To achieve improved accelerating gradients at increased operating temperatures (> 4 K), efforts are underway to coat Nb SRF cavities with Nb_3Sn thin films. However, the accelerating performance of Nb_3Sn coatings fabricated using the vapor deposition procedure is limited by the surface roughness and presence of near-surface defects such as atomic dislocations, inhomogeneities, and high grain boundary densities. This experimental study aims to identify the relationships between Nb$_3$Sn growth parameters such as the Sn flux, Nb oxide content, Nb defect density, and annealing temperatures both during and post-deposition on the resultant Nb-Sn-O surface interactions that dictate alloy morphology.

Using a well-characterized (3×1)-O/Nb(100) single crystal, Sn deposition was done in an ultra-high vacuum chamber equipped with *in situ* surface characterization techniques including Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy. To induce alloy formation, the (3×1)-O/Nb(100) surface was exposed to precise monolayer equivalences of Sn (10.0 - 20.0 ML) and subsequently annealed between 500 – 1000 °C. Results suggest that the substrate deposition temperature and Nb oxide morphology are two of the most significant factors affecting both the persistence of Sn on the Nb substrate as well as Nb-Sn-O oxidation behavior. AES data demonstrate that Sn deposition on an 800 °C substrate suppresses Sn desorption during 800 - 1000 °C post-deposition anneals. Furthermore, XPS data distinguish the relationship between the oxidation state of Sn adlayer contributions and the resultant Sn desorption behavior. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor deposition conditions on the growth mechanisms and alloying dynamics that ultimately enable pristine Nb$_3$Sn growth.

SS-Contributed On Demand-67 Reactions of Boron-containing Molecules with H- and Cl-terminated Si(100)*, Dhamelyz Silva Quinones,* *A. Teplyakov,* University of Delaware*; R. Butera,* Laboratory for Physical Sciences*; G. Wang,* Sandia National Laboratories

The reactions of boron trichloride, boric acid and 4-fluorophenylboronic acid in solution were studied in order to understand the interaction of these molecules with hydrogen- and chlorine terminated Si(100) surfaces prepared in solution. The reactions were mainly followed by X-ray photoelectron spectroscopy (XPS) which shows that these molecules react preferentially with Cl-Si(100) compared with H-Si(100) at similar conditions. Within the range of reaction conditions investigated, boron trichloride reacts preferentially with the Cl-terminated surface compared to H-terminated surface. On this Cl-Si(100) surface, the direct Si-B direct bond is formed as confirmed by XPS. At 70°C, the reaction loses its selectivity and both surfaces form B-containing surface species. Boric acid and 4-fluorophenylboronic acids react selectively with Cl-Si(100) surface, introducing boron onto the surface and forming a Si-O-B structure. The quantification of boron surface coverage demonstrates that the 4-fluorophenylboronic acid leads to ~3 times higher boron coverage compared to boric acid on Cl-Si(100). Density functional theory was utilized to identify possible major surface species resulting from these reactions and to supplement the experimental findings, showing that the reactions of boric acid and 4-fluorophenylboronic acid are more favorable with the Cl- versus H- terminated surface, and on Cl-Si(100) the reaction with 4-fluorophenylboronic acid is more thermodynamically favorable than the reaction with boric acid. This work provides a new pathway to obtain a functionalized silicon surface with a direct Si-B bond and boron incorporation into silicon surface via Si-O-B bonds that can be used for further functionalization or as a means of selective-area monolayer doping.

SS-Contributed On Demand-70 2020 AVS Dorothy M. and Earl S. Hoffman Scholarship Award Talk: Ru Precursors for Photoassisted Chemical Vapor Deposition: Comparison of Allyl and Diene Complexes*, Christopher Brewer*[1], *N. Sheehan,* University of Florida*; B. Salazar,* University of Texas at Dallas*; J. Herrera,* University of Florida*; A. Walker,* University of Texas at Dallas*; L. McElwee-White,* University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, such as (η^3-allyl)Ru(CO)$_3$X (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Quantum yields for loss of a single CO ligand in alkane solutions were determined for the (η^3-allyl)Ru(CO)$_3$X complexes, to elucidate the photochemistry that initiates the deposition process. As a comparative study, the quantum yields for various (diene)Ru(CO)$_3$ complexes were determined. These (diene)Ru(CO)$_3$ undergo mixed photolytic decomposition pathways, making them attractive precursors for photochemical CVD. This talk will discuss the photochemistry of the (diene)Ru(CO)$_3$ complexes relative to the (η^3-allyl)Ru(CO)$_3$X complexes with respect to their deposition results.

SS-Contributed On Demand-73 Thermal Atomic Layer Etching of CoFeB Alloy Thin Films Using Chlorine and Acetylacetone (acacH)*, Mahsa Konh,* *A. Teplyakov,* University of Delaware

The mechanism and efficiency of thermal dry etching of CoFeB alloy thin films using Cl$_2$ and 2,4-pentanedione (acetylacetone, acacH) were investigated. CoFeB alloy is commonly used in magnetic random-access memory (MRAM) technology. The initial steps of etching were followed by detecting expected desorbing fragments during a linear heating ramp via temperature-programmed desorption (TPD). The chemical composition of the etched surfaces was then analyzed ex situ with X-ray photoelectron spectroscopy (XPS). The etch rate was measured by comparing the film thickness before and after ALE process using atomic force microscopy (AFM) of patterned samples. The overall mechanism of thermal etching on the alloy thin films is quite complicated as the desorbing metal-containing products have the overall formula M(acac)$_x$Cl$_y$; however, it appears that the process does not affect the surface concentrations of the alloy constituents.

SS-Contributed On Demand-76 Following the Microscopic Pathways to Energy Dissipation and Adsorption in Molecule-Metal Surface Encounter*, Igor Rahinov,* The Open University of Israel*; D. Borodin,* University of Göettingen, Germany*; P. Shirhatti,* Tata Institute of Fundamental Research, India*; M. Huang,* University of New Mexico*; A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry, Germany*; D. Auerbach,* Max Planck Institute for Biophysical Chemistry*; T. Zhong,* Max Planck Institute for Biophysical Chemistry, Germany*; H. Guo,* University of New Mexico*; D. Schwarzer,* Max Planck Institute for Biophysical Chemistry, Germany*; T. KItsopoulos, A. Wodtke,* University of Göettingen, Germany

The most common mechanism of catalytic surface chemistry is that of Langmuir and Hinshelwood (LH). In the LH mechanism, reactants adsorb, thermalize with the surface and subsequently react. At the same time, molecular vibration is known to enhance the rates of gas-phase chemical reactions as the motion associated with bond stretching facilitates the reactant molecule approach to the transition state [1]. However, for reactions occurring on via LH mechanism on metal surfaces, relevant for heterogeneous catalysis reactions, the ability of vibrational excitation to promote reactivity is hampered by rapid dissipation of the vibrational energy of the reactant into electronic excitation of the metal within several picoseconds [2]. Our recent findings challenge this paradigm: we have demonstrated that excited vibrational states can survive longer than expected [3,4] – suggesting vibrational excitation might promote or modify heterogeneously catalyzed LH-chemistry on metals. In our experiments IR laser excitation was used to prepare short pulses of vibrationally excited CO(v=2) molecules that impinged and scattered from clean Au(111) surface. By quantum-state-resolved scattering studied in temporally and spatially resolved fashion we have unambiguously demonstrated that vibrationally excited molecules, prepared in the v=2 state retain significant vibrational excitation, even after residing ~ 50 ps on Au(111). Furthermore, we show that the vibrational relaxation time can serve as an internal clock to follow the microscopic pathways of adsorption and equilibration on the surface. On the basis of molecular beam experiments and theoretical modeling we reveal the intricate interplay between physisorption and chemisorption states for the prototypical CO/Au(111) system, relevant to many other heterogeneous systems.

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SS-Contributed On Demand-79 In Situ Observations of Graphene Growth on Liquid Copper*, Irene Groot,* Leiden University, The Netherlands

Since its first preparation a decade ago, graphene has been a promising material for many technological applications, due to its unique physical and

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[1] **AVS 2020 Dorothy M. and Earl S. Hoffman Scholarship Awardee**

chemical properties. However, until today graphene cannot be found yet in the devices it seems so suitable for. The reason is that the production of large sheets of defect-free graphene at time scales compatible with an industrial process has not yet been achieved. Defects in the graphene result from the grain boundaries and defects that are present at the surface of the catalyst used: solid copper. Recently, it was found that large sheets of defect-free graphene can be grown on liquid copper instead [1]. Liquid copper has a smooth surface without the defects present in solid copper, and the mobility of graphene on the liquid surface enables a fast growth process and the healing of defects. All research so far on graphene growth on liquid copper, however, has been performed after the growth and after the cooling down of the copper-graphene system to room temperature, introducing changes to the structure of graphene.

In this talk I will show the reactor that we have developed to investigate the growth kinetics of graphene on liquid copper at 1400 K *while the process is taking place*. We make use of Raman spectroscopy, optical microscopy, grazing-incidence X-ray diffraction, X-ray reflectivity and theoretical calculations to understand and tune the graphene growth. By tuning the reaction conditions during growth, we are able to grow millimeter-sized single-crystalline graphene sheets of the highest quality with a growth speed of ~ 1 micrometer/s, paving the way for their use in a range of optoelectronics applications.

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement 736299.

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SS-Contributed On Demand-82 Laser-Photoemission Electron Microscopy —Deciphering the Morphology of Semi-Crystalline Polymer Films

Falk Niefind, Physical Measurement Laboratory, National Institute of Standards and Technology (NIST)*; S. Mannsfeld,* Technische Universität Dresden, Germany*; S. Karande, A. Kahnt, B. Abel,* Leibniz Institute of Surface Engineering (IOM), Germany

Reducing mankind's carbon footprint in a quest to combat climate change is one of the biggest challenges for humanity in the current century. Decarbonization of the energy sector by increasing the contribution of renewable energy sources is one vital step on this path.[1] Organic solar cells or organic photovoltaics (OPV) based on thin polymer films can play a vital role in tackling this challenge. Their appeal derives from their unique properties when compared to classical silicon-based photovoltaics: their chemical composition, mechanical properties as well as their optical characteristics can be tailored to the specifics of the area of application (e.g. walls, windows, roofs and cars).[2] However, the performance of polymer OPV devices is closely linked to the nanoscale morphology (e.g. the polymer orientation, domain size and local crystallinity) of the polymer films.[3] Thus, gaining insight into said morphology has attracted significant interest during the last decades. Traditionally, the morphology is controlled via the fabrication method such as spin coating or doctor blading as well as the fabrication parameters such as temperature, printing speed and solvents used. We present an imaging technique based on a photoemission electron microscope (PEEM) and a linearly polarized femtosecond laser system, all in tabletop format. The method can determine the polymer orientation, domain size and local degree of order in a single straight forward imaging measurement, with a spatial resolution of up to 50 nm. Our method exploits a two-photon photoemission (2PPE) process that exhibits a dichroism with respect to the linear polarization of the employed laser light and the polymer backbone. Our experiments were conducted on Poly(3-hexylthiophene-2,5-diyl) (P3HT), a benchmark polymer in the OPV community.[4,5,6]

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SS-Contributed On Demand-85 Thermal Oxidation of Ru(0001) to RuO_2 Studied With Ambient Pressure X-ray Photoelectron Spectroscopy

J. Trey Diulus, *Z. Novotny, B. Tobler,* University of Zurich, Switzerland*; L. Artiglia, J. Raabe,* Paul Scherrer Institute, Switzerland*; J. Osterwalder,* University of Zurich, Switzerland

Ruthenium dioxide (RuO_2) is known to be a highly efficient oxidation catalyst for heterogeneous reactions. Understanding the formation of late transition metal oxides from a fundamental approach is imperative for the heterogeneous catalysis community and can lead to improved catalyst designs.[1] Surface science literature has previously proposed from thermal desorption spectra and theory that the formation of an O-Ru-O tri-layer or RuO_x suboxides are involved in creating RuO_2, although studying the chemical state of these intermediate oxides has proven difficult.[1,2] In this study, we report on the thermal oxidation of single-crystalline Ru(0001) films *in-situ* during time-lapsed ambient pressure X-ray photoelectron spectroscopy (APXPS) measurements. As received samples were inserted into an APXPS endstation,[3] composed of a 200 nm thick Ru(0001) film deposited on a yttria-stabilized-zirconia film on top of a Si(111) substrate. Samples were treated with thermal annealing in high vacuum (HV, 10^{-7} mbar) or 0.01 mbar of oxygen and crystallinity was verified with low energy electron diffraction. During thermal oxidation, samples were exposed to a constant pressure of 0.01 mbar as the temperature was increased stepwise. At 200 ºC, we observe adventitious carbon contamination burned away, followed by a coexistence of Ru and Ru-O peaks in the Ru 3d and O 1s core levels after further heating to 300 ºC, indicating the presence of a O-Ru-O tri-layer. After 1.5 hours at 350 ºC, the metal component of the Ru 3d spectra becomes negligible and a shift in binding energy occurs in the O 1s spectra. Additionally, a satellite forms at 285 eV in between the Ru $3d_{5/2}$ and $3d_{3/2}$, characteristic of RuO_2. Furthermore, with quantitative analysis, we calculated the stoichiometry of the formed oxide film, thus providing evidence for a model pathway of the oxidation of Ru(0001).

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SS-Contributed On Demand-88 STM Study of Ag Encapsulation of Pd Islands on Ag(111)

Buddhika Alupothe Gedara, *M. Muir, M. Trenary,* University of Illinois at Chicago

PdAg bimetallic heterogenous catalysts play a vital role in the petroleum and chemical industries as they can enhance both activity and selectivity of hydrogenation reactions. For further development of PdAg catalysts, it is important to understand their atomic-scale behavior. We have studied Ag encapsulation of Pd islands at three different Pd coverages (0.028, 0.064, and 0.135 monolayer (ML)) on Ag(111) at room temperature (RT) using scanning tunneling microscopy. While previous studies have shown that the structure and composition of Pd islands on Ag(111) change at elevated temperatures, we found that surface Ag atoms cover the Pd islands even at RT. Our results suggest that these Ag atoms migrate to the top of the Pd islands through special defects identified as stacking fault tetrahedra (SFT), such as has been reported in previous studies on Au(111). Furthermore, we have studied the behavior of the islands upon annealing. The majority of the Pd islands are encapsulated by surface Ag atoms at 350K to form a Ag/Pd/Ag(111) structure. However, upon further annealing we observed that the composition of some islands at a 0.135 ML Pd coverage changed to Ag/Ag/Pd/Ag(111). This study reveals how surface Ag atoms migrate to encapsulate Pd islands.

SS-Contributed On Demand-91 An Xps Study of the Interaction between the Uranyl Ion and Oligoarginine Peptide

Esha Mishra, *C. Schultz,* University of Nebraska - Lincoln*; P. Dowben,* University of Nebraska–Lincoln*; R. Lai,* University of Nebraska - Lincoln

X-ray Photoemission Spectroscopy (XPS) was used to analyze oligoarginine polypeptide, with methylene blue on a gold substrate. The X-ray photoemission of these oligoarginine polypeptides before and after exposure to U(VI), i.e., uranous oxide, was compared. For the N 1s core level spectra, the shift of N 1s peak towards the lower binding energy was observed after the oligoarginine polypeptide was exposed to U(VI). This result suggested that there is a charge donation to the polypeptide, through the polypeptide backbone and the amine in the polypeptide is not bonding to the UO_2 oxygen, but to the uranium itself. XPS core level spectra for uranium U $4f_{7/2}$ suggested that the uranium is bonded to the oligoarginine peptide, with some back charge donation, likely related to some oligoarginine polypeptide interaction with the oxygen, to partly reduce the UO_2 moiety. We find that not all short-chain polypeptide binds effectively with U(VI), i.e., uranous oxide. This work expands XPS studies of heavy metal biomolecule interactions from interactions with deoxyribonucleic acid (DNA) to proteins and shows the utility of the technique in filling out the coordination chemistry picture.

SS-Contributed On Demand-94 Surface Stability, Phonon Band Structure, and Vibrational Dynamics of the Nb(100) Surface Oxide Reconstruction*, **Alison McMillan**, C. Thompson, J. Graham,* University of Chicago*; M. Kelley,* Cornell University*; S. Willson, R. Farber,* University of Chicago*; T. Arias,* Cornell University*; S. Sibener,* University of Chicago

Niobium's fundamental properties have led to its use in most modern superconducting radio frequency (SRF) cavities in particle accelerators, but these cavities now are approaching the performance limits of Nb. Future progress must come from the development of new materials: one promising alternative is Nb_3Sn. Nb_3Sn thin films generally are formed on bulk Nb samples, and their growth is dictated by the interaction of Sn with the Nb surface. Nb, however, has a strong affinity for oxygen; it almost always is covered by an oxide layer. An in-depth description of the oxide surface, then, is essential for improving Nb_3Sn growth procedures. This combined study, with helium atom scattering (HAS), Auger electron spectroscopy (AES), and density functional theory (DFT), investigates the microscopic structure and dynamics of the (3x1)-O surface reconstruction of Nb(100). High-resolution He diffraction and line-shape analysis, confirmed by AES, reveal that the (3x1)-O surface is stable up to at least 1130 K. The atomic-scale surface structure, composition, and coherence do not change over a wide range of temperatures, including the temperature at which Nb typically is held during Sn nucleation. Inelastic He time-of-flight measurements are used to map out the phonon band structure of the Nb(100) oxide and determine the nature of the surface vibrational dynamics. DFT calculations of the phonon band structures for both the metallic and oxidized Nb(100) surfaces show the effect of the oxide on the electronic structure and bonding at the surface and corroborate HAS data. These results impact the current understanding of the oxide covered Nb surface – critically needed information for furthering our understanding of Nb alloy formation – and aid the development of new SRF technologies.

SS-Contributed On Demand-97 Evidence of a Surface to Bulk Core Level Shift in $CoFe_2O_4$ Thin Films Grown on Al_2O_3*, **Arjun Subedi**, Y. Yun, D. Yang, X. Xu, P. Dowben,* University of Nebraska-Lincoln

We find evidence for a surface to bulk core level shift in both the Co 2p and Fe 2p core level photoemission spectra of 5.5 nm $CoFe_2O_4$ (111) film grown on Al_2O_3 (0001). The Co $2p_{3/2}$ and Fe $2p_{3/2}$ surface components were distinguished from the bulk components by angle resolved X-ray photoemission spectroscopy (ARXPS). While many complex oxides show a strong preferential surface termination, the surface termination of $CoFe_2O_4$ (111) contains both Co and Fe, but the core level photoemission binding energy shifts tend to indicate that the surface is significantly different from the bulk, even for so thin a film. Furthermore, X-ray photoemission spectroscopy (XPS) measurement of 1.7 nm $CoFe_2O_4$ (111) film grown on Al_2O_3 (0001) shows a suboxide interlayer of cobalt. We compare the surface properties of $CoFe_2O_4$ thin films with that of $NiFe_2O_4$ thin films. This has implications for cobalt ferrite as a magnetic storage media and could affect growth of this spinel in the degradation of steel in boiling water nuclear power applications.

SS-Contributed On Demand-100 Chemistry of Titanium Deposition Precursors for Area-Selective Deposition on Functionalized Silicon*, **Tyler Parke**, D. Silva-Quinones,* University of Delaware*; G. Wang,* Sandia National Laboratories, USA*; A. Teplyakov,* University of Delaware

Atomically precise and area-selective deposition processes are vital to the miniaturization of devices in modern electronics. Here, the selectivity of the titanium atomic layer deposition (ALD) precursors, $TiCl_4$ and TDMAT (tetrakis(dimethylamido)titanium), on hydroxyl, hydrogen, and chlorine-terminated Si(111) and Si(100) surfaces was investigated. Ex situ X-ray photoelectron spectroscopy (XPS) demonstrated that $TiCl_4$ readily deposits on HO-Si and to a lesser degree, on H-Si, but is relatively inert to Cl-Si. Atomic force microscopy (AFM) showed growth of smooth films on HO-Si, but delayed nucleation onto hydroxyl- containing defects in the H-Si surface. Density functional theory (DFT) simulations suggested the favorable chemisorption of $TiCl_4$ onto hydroxyl-containing surfaces in HO-Si and defected H-Si models. Thermal atomic layer deposition of TiO_2 with $TiCl_4$ and water on these surfaces was also compared with a commercial ALD process utilizing TDMAT and water.

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SS-Contributed On Demand-103 GRISU – Bonds in Focus*, **David Rath**, J. Pavelec, G. Parkinson, M. Schmid, U. Diebold,* TU Wien, Austria

The IRAS system GRISU (**GR**azing incident **I**nfrared absorption **S**pectroscopy **U**nit) was developed for investigations of adsorbates on oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with an UHV chamber [1]. All the optical components are mounted precisely in respect to each other to ensure the high performance requirement also after long term use, and the compact design requires just one CF150 flange (8" O.D.) on the UHV chamber.

The system features five mirrors for beam guidance placed in HV and UHV environment, and optimises the system's performance, flexibility and usability. Two of these mirrors are mounted on motorised kinematic mounts. One aperture allows to control the shape of the illumination area on the sample to reduce the background signal. A second aperture limits the incidence angle range of the infrared radiation illuminating the sample. Incidence angles between 49 ° and 85 ° are possible. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample.

The simulated system (done with a ray tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e. 13 % of the radiation passing through the first aperture (Ø 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, this is higher by a factor of about 20.

[1] J. Pavelec, et al., J. Chem. Phys. 146, 014701 (2017).

SS-Contributed On Demand-106 RRKM Treatment of HCl Dissociative Chemisorption on Au(111): Reactive Dampening through Inefficient Translational Coupling and an Active Surface*, **Mark Bernard**, I. Harrison,* University of Virginia

Microcanonical unimolecular rate theory is applied to Shirhatti *et al.'s* recent supersonic molecular beam experiments examining the activated dissociative chemisorption of HCl on Au(111). A precursor mediated microcanonical trapping (PMMT) model [where the surface vibrates and HCl rotations, vibration, and translation directed along the surface normal are treated as active degrees of freedom] gave dissociative sticking coefficient predictions that are several orders of magnitude higher than experimental values, but in good accord with prior quantum and molecular dynamics simulations. Density functional theory electronic structure calculations using the PBE functional served to fix the vibrational frequencies of the reactive transition state and the threshold energy for dissociation, E_0 = 72.9 kJ/mol. To explore the possibilities of varying threshold energy, coupling to phonons, and dynamics, a three-parameter [E_0, s, ε_n] dynamically-biased (d–) PMMT model was fit to the experiments. A dynamical bias was introduced using an efficiency, ε_n, of normal translational energy to contribute to the active exchangeable energy capable of promoting reactivity. To achieve the low sticking probabilities observed in experiment, severe normal translational energy dampening ($\varepsilon_n \rightarrow 0.38$) was imposed, leading to a large vibrational efficacy of $h_v=e_v/e_n=2.6$. Despite this high vibrational efficacy, the experiments were relatively insensitive to vibrational energy at all but the lowest normal translational energies.The optimal threshold energy for dissociation was E_0 =31.8 kJ/mol, some 41 kJ/mol below the PBE-DFT prediction. Increasing the number of Au surface oscillators, s, capable of exchanging energy with HCl in the transient collisionally formed precursor complexes, correlated to a decrease in dissociative sticking at all translational energies, designating lattice vibrations as a dissipative channel. The d-PMMT modeling indicates that the HCl/Au(111) reactivity may be consistent with electronically adiabatic passage across a relatively low and late transition state that dynamically disfavors normal translational energy and admits energy dissipation to phonons.

SS-Contributed On Demand-109 Fast Diffusive Behavior of Pb on Ge(111) at Low Temperatures During Island Formation*, **Andrew Kim**, E. Baum, S. Chiang,* University of California at Davis*; M. Tringides,* Ames Laboratory, Iowa State University*; V. Stroup, D. Le, A. Childs, T. Rahman,* University of Central Florida

Lead deposited on Ge(111) at low temperatures (200-273K) was found to show unusual collective diffusion behavior after achieving a critical coverage (about 1.5ML). Depending on the temperature of the sample at the time of deposition, the size and number density of the Pb nucleated islands vary. From LEEM real time images, a high rate of movement of Pb atoms was found at the beginning of island formation, which was too fast to be explained by thermal diffusion. In order to measure the diffusion barrier of this unusual process, experiments were performed to follow the growth of these islands, with additional deposition beyond the critical coverage at constant temperature. Similar behavior was seen with Pb on Si(111) at low temperatures,[1] with island formation whose heights were determined by quantum size effects,[2] as well as unusually fast diffusion speed.[3] In order to explain the diffusing behavior of Pb, we also present a first-principles study of the structure of Pb overlayers on Ge(111) using DFT calculations, which were inspired by experimental observations of Pb/Ge(111) phases.[4]

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[2] M. Hupalo et al., Surf. Sci. 493, 526 (2001).

[3] M. Hupalo and M. C. Tringides, Phys. Rev. B 75, 235443 (2007).

[4] Y. Sato and S. Chiang, Surf. Sci. 603, 2300 (2009)

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SS-Contributed On Demand-112 Selective Catalytic Chemistry at Rhodium (II) Nodes in Bimetallic Metal–Organic Frameworks*, Deependra Shakya*, *D. Chen, O. Ejegbavwo, N. Shustova,* University of South Carolina*; K. Vogiatzis,* University of Tennessee Knoxville*; A. Frenkel,* Stony Brook University/Brookhaven National Laboratory*; S. Senanayake,* Brookhaven National Laboratory*; A. Brandt,* University of South Carolina*; A. Ebrahim,* Stony Brook University/Brookhaven National Laboratory

Gas-phase catalytic activity has been studied at the metal nodes of metal-organic frameworks (MOFs), which provide the ability to control the geometry and ensemble size of active metal sites. We report one of the first studies of a gas-phase reaction catalyzed by isolated, highly dispersed sites at the metal nodes of a crystalline metal-organic framework (MOF). $(Cu_xRh_{1-x})_3(BTC)_2$ (abbreviated CuRhBTC, where BTC^{3-} =benzenetricarboxylate) is prepared from Rh^{3+} and CuBTC (HKUST-1) by post-synthetic ion-exchange. X-ray photoelectron spectroscopy and X-ray absorption near edge structure (XANES) were used to identify the oxidation state of Rh in CuRhBTC as +2. These Rh^{2+} sites are active for the catalytic hydrogenation of propylene to propane at room temperature, and the MOF structure stabilizes the Rh^{2+} oxidation state under reaction conditions. Scanning transmission electron microscopy experiments indicate that the Rh ions are uniformly dispersed on the nanoscale, and Raman spectroscopy studies demonstrate that bimetallic Cu-Rh nodes are formed. Density functional theory calculations suggest a mechanism in which H_2 dissociation and propylene adsorption occur at the Rh^{2+} sites.

SS-Contributed On Demand-115 Electron Stimulated Desorption from Ethane Condensed on Rare Gas Surfaces*, Sramana Kundu*, *M. Schaible, T. Orlando,* Georgia Institute of Technology, USA

The process of desorption induced by electronic transitions (DIET) is important in surface chemistry and physics. It is relevant in almost every system where solid surfaces are impacted by energetic particles, like surface modification processes in the laboratory to cold dust grains exposed to ionizing radiation in the interstellar medium. Study of such processes can help us understand chemical bonding on surfaces, charge and energy transfer, conversion of electronic energy to kinetic energy of the adsorbate, etc. Analysing the cations generated by electron stimulated desorption (ESD) from the adsorbed molecule is one way to do that. In general, fragmentation and ion desorption from species adsorbed on metals are quenched due to interactions with the metal substrate. Depositing the molecules on multilayers of rare gases overcomes this problem by localizing the electronic excitation on the adsorbate. The use of different rare gases – argon, krypton and xenon – leads to differences in the fragmentation and desorption processes of the same adsorbate, revealing how energy exchange occurs in each case.

Sub-monolayer quantities of ethane (C_2H_6), the simplest hydrocarbon with C–C and C–H bonds, was deposited on about 50 monolayer (ML) thick rare gas adsorbed on Ag substrate held at ~14 K in an ultra-high vacuum (UHV) chamber (base pressure = 5×10^{-10} torr). The sample was irradiated with electrons of specific energy using a pulsed electron gun. The positive ions are collected and analysed with a time-of-flight mass spectrometer (TOFMS) with a multichannel plate (MCP) detector. Mass spectra is collected at several energies between 15 and 50 eV and compared.

The threshold electron energy for ions generated from ethane is 15 eV for Ar and Kr, and 17 eV for Xe. The ion intensities from the rare gases follow the order Ar > Kr > Xe for the entire range we studied. The most likely mechanism is the ionization of the rare gas followed by charge transfer from the rare gas to ethane, causing its ionization and fragmentation. The ionization energy gap between the rare gases and ethane is in the order Ar > Kr > Xe, which is reflected in the ion intensities from the respective rare gas. The branching ratios of the observed ions - CH_3^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ and $C_2H_6^+$ - are calculated at each energy. $C_2H_4^+$ is the most intense fragment in the mass spectra in the threshold region (15-20 eV) for all three rare gases. The ratios change with energy and with the identity of the rare gas. This is because the energy available for the formation and subsequent desorption of a given fragment ion depends on the energy transfer process with the rare gas on which the molecule resides.

SS-Contributed On Demand-118 Investigation of the Initial Stages of Iron Surface Oxidation and Corrosion at the Liquid/Solid and Gas/Solid Interface Using *in situ* Surface Spectroscopy*, Chathura de Alwis,* *M. Trought,* Michigan Technological University*; S. Nemsak,* Advanced Light Source, Lawrence Berkeley National Laboratory*; K. Perrine,* Michigan Technological University

Redox reactions of iron and their oxides maintain the balance of water, mineral and plant nutrient cycles on earth. Iron corrosion is a spontaneous electrochemical process, where iron serves as the anode and water and O_2 drive the cathode reaction. Ions, such as chlorides, are known to catalyze the surface reduction-oxidation reaction of iron and initiate the corrosion by breakdown of the native oxide layer. The rate of corrosion and the chemical composition of mineral scale formed at the metal surface depends upon the chemical environment of the electrolyte. Alkali chlorides catalyze surface oxidation of iron leading to the corrosion and metal degradation forming complex oxide films as the major products of corrosion.

To address these complex reactions, we developed a method utilizing polarized modulated infrared reflection absorbance spectroscopy (PM-IRRAS) and the meniscus method with our custom-build liquid cell to investigate the real-time redox processes at air/electrolyte/iron interfaces. This technique allows for probing the air/liquid/solid interface simultaneously of spontaneous redox reactions as a function of time under ambient conditions. In this study, a NaCl(aq) electrolyte was used as a model system as part of the air/electrolyte/iron interface. The interfacial oxidation of iron and mineral formation was strongly affected by the chemical properties of electrolyte. A considerable difference was observed at the interface, where the chemical composition of the minerals grown from gradual exposure to atmospheric O_2 and CO_2 compared to the fully submerged region of iron in NaCl(aq) with limited exposure to air (O_2 and CO_2). These results were supported with *ex situ* ATR-FTIR and XPS analysis.

These studies were compared to the initial stages of iron oxidation using ambient pressure (AP)-XPS at the gas/solid interface. A droplet of NaCl(aq) was exposed to the iron surface and then oxidized with various pressures of water and O_2 up to 100 mTorr. It was found that surface carbonate was produced, primarily from the combined oxidation of surface hydrocarbons, and a corresponding change in the anion/cation ratio. These studies of the initial stages of iron surface oxidation at the air/liquid/solid interface and the gas/solid interface advance our understanding of how ions from NaCl(aq), O_2 and H_2O affect the corrosion mechanism. This research suggest that ions play a critical role in the various stages of corrosion and the resulting mineral formation that impact environmental processes.

SS-Contributed On Demand-121 STM Studies of Alkanethiolate Reactivity with Atomic H as a Function of Temperature & Chain Length*, Sarah Brown*, *J. Sayler, S. Sibener,* University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species yield important information about gas-surface interactions in organic films, specifically how static and dynamic disorder influence passivation. We have investigated the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunnelling microscopy (UHV-STM). First, a series of alkanethiolate samples of varying chain length (8- to 11-carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. It was found that small increases in chain length caused disproportionately large decreases in reactivity at room temperature. This reaction progression was described using an exponential model containing two rate constants: a slow rate for hydrogen reactivity with standing-up phase, which is dependent on chain length, and a fast rate for low-density phase reactions, which is the same for all samples.

Chain length-dependent changes in surface morphology were also observed, with short chain SAMs experiencing significant vacancy island reconstruction throughout the reaction compared to longer chain SAMs. Finally, the effect of temperature on the reactivity of decanethiolate SAMs was studied by reacting them with H at lower temperatures (130 K, 250 K and 270 K). The SAMs' reactivity was greatly reduced at lower temperature, with longer reaction times for 270 K and 250 K, and no visible reaction occurring at 130 K. Furthermore, there was a noticeable change in the reaction mechanism at 250 K, indicated by the fact that the originally-proposed two-rate constant model could not describe the 250 K experimental data. The changes in surface morphology during the reaction also differed significantly at 250 K. Reduced thiol mobility, lower surface energy, and increased lateral forces between chains at lower temperature are proposed to contribute to these changes in reactivity.

SS-Contributed On Demand-124 Surface Chemistry of 2-Propanol on SnO_2(101) Studied Using Ambient-Pressure X-Ray Photoelectron Spectroscopy

Jessica Jenkins, *R. Elzein, R. Addou, G. Herman,* Oregon State University

Tin dioxide (SnO_2) surface terminations can strongly impact surface reducibility especially under vacuum at different temperatures. For SnO_2 surfaces, tin ions can be in either the Sn^{4+} or Sn^{2+} oxidation state and this provides flexibility in controlling defect chemistries and catalytic properties. For example, studies have shown that the Sn^{+4}/Sn^{+2} ratio can significantly impact the activity of CO oxidation on SnO_2 nanomaterials. SnO_2(110) and SnO_2(101) surfaces have significantly different surface structures and temperatures where the surfaces become reduced in vacuum. Prior studies using low energy ion scattering indicated that the SnO_2(110) and SnO_2(101) initially had changes in their surface composition at ~440 and ~550 K, respectively. Recently we have shown that the reaction of 2-propanol on SnO_2(110) follows a Mars−van Krevelen reaction mechanism, where surface oxygen vacancies are formed during the surface reaction with 2-propanol. For this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and low energy electron diffraction (LEED) to characterize the SnO_2(101) surfaces and used AP-XPS and *in situ* mass spectrometry to characterize the oxidation reactions. Experiments were performed on the SnO_2(101) surface for 2-propanol pressures up to 1 mbar, various 2-propanol/O_2 ratios, and a range of temperatures. During this presentation we will compare our experimental results to those we have previously obtained from the SnO_2(110) surface and relate these to the observed chemistries and the differences in surface structure.

SS-Contributed On Demand-127 Bi-Induced Shape Change of Homoepitaxial InAs(110) Surface Structure

Brandon Carter, *J. Millunchick,* University of Michigan

Bi surfactants have a profound effect on the surface morphology of III-V semiconductors [1]. They induce a large anisotropy in adatom diffusivity on (001) GaAs surface, which can either smoothen films or cause mounding along the [1-10] [2]. Bi surfactants are also used to drive the self-assembly of (110) InAs quantum dots on GaAs(110) by changing the growth mode from 2D to 3D [3]. This work examines the Bi-induced change in surface morphology on homoepitaxial InAs(110), by growing 20 period InAs:Bi superlattices at T=290°C. Each period consisted of 30nm of InAs followed by exposure to Bi flux for times 0<t<45s. The top surfaces of the films were characterized using tapping mode atomic force microscopy. During homoepitaxial growth, large faceted trapezoidal mesas ~4 µm in diameter and 340 nm tall form on the surface with flat regions in between. The parallel edges of the trapezoid are aligned perpendicular to the [001], while the side legs are aligned along the [1-1-3]and [-11-3]. The morphology between the mesas is defined by a scalloped, or semicircular, step structure that is relatively flat, with root mean squared (RMS) roughness of 14 nm. At a Bi exposure of t=15s, the mesas shrink both in diameter and height and the background roughens such that RMS=55nm. But as more Bi is deposited, the surface smooths such that at t=45s RMS=24nm. The mesas also undergo a Bi-induced shape change; specifically, the alignment of the trapezoidal legs start to shift towards lower indices beginning at t=15s and becoming more prominent as more Bi is deposited, such that the legs align along the [1-1-1] and [-11-1] at t=45s. Closer analysis reveals that the changes in surface roughness and island shape are related to a change in step structure. Without Bi the steps perpendicular to the [001] are straight and are comprised of bunches ~19 nm tall. However, the steps unbunch as Bi is deposited with step bunching height ~3nm tall at t=45s. The steps also begin to meander with the addition of Bi. Bi does not form droplets on these surfaces, in contrast to reports of growths on the (001) InAs surface [4], thus leading to higher Bi incorporation on the (110) compared to the (001) . These observations together show that the energetics of the (110) are vastly altered by Bi and may suggest an atomic mechanism for surface segregation.

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SS-Contributed On Demand-130 Patterned and Graded ALD Coatings for Imaging and Spectroscopy Applications

April Jewell, *J. Hennessy, S. Nikzad,* Jet Propulsion Laboratory

We present an overview of our work using atomic layer deposition (ALD) to develop optical coatings for silicon detectors. To date, our team has taken advantage of the spatial uniformity of ALD for device passivation, antireflection coatings, and optical filters. Our current work is aimed at introducing spatially varying detector response spanning the ultraviolet (UV) and visible wavelength ranges. Intentionally introduced spatial non-uniformities (i.e. patterning) in a coating, for example, would allow one to match a detector's spatial response relative to the incident wavelength for spectrograph applications.

Two approaches will be discussed, including Area Selective (AS) and Spatial (S) ALD. We report on an AS-ALD investigation on the patterning of aluminum fluoride (AlF_3) antireflection coatings. We explored AlF_3 deposition directly on bare silicon and on silicon pre-coated with lithium fluoride (LiF). We examined the effect of different aluminum precursors, including trimethylalumnium (TMA), triethylaluminum (TEA), dimethylaluminum hydride (DMAH), and hexakis (dimethylamino) dialuminum (TDMAA); in all cases the F precursor was hydrofluoric acid (HF). We show that the TMA/HF ALD reaction was completely inhibited when attempting to deposit AlF_3 films directly on LiF; while the other precursors showed varying levels of inhibition. We also use SALD to develop coatings with a graded thickness across a detector surface, which could potentially result in more subtly varying transitions in detector response from one end to the other.

When combined with JPL's delta-doped silicon detector technology, the development will result in detectors with high quantum efficiency (QE) in targeted wavelength bands, allowing for more versatile UV–Visible instrumentation including spectrometers. The advancement will enable more affordable, and less complex, high-performance instruments and thus addresses NASA's strategic objectives.

SS-Contributed On Demand-133 Beyond the Ligand Exchange Model – Time Resolved ALD of HfO2 on InAs Thermal Oxide

Giulio D'Acunto, *P. Shayesteh, F. Rehman,* Lund University, Synchrotron Radiation Research, Sweden*; E. Kokkonen,* MAX IV Laboratory, Lund University, Sweden*; R. Timm, J. Schnadt,* Lund University, Synchrotron Radiation Research, Sweden

Atomic layer deposition (ALD) is a powerful technique for the highly controlled deposition of thin-film materials. Its parent techniques, chemical and physical vapor deposition, have been popular for a long time. In contrast, ALD – invented in the 1960s & 1970s – has become increasingly important only since the turn of the new century. This is illustrated by the fact that 18,000 studies on ALD have been published during the past two decades. In the past five years even an average of 1,500 publication per year has been recorded. Thus, nowadays ALD is central to a wide range of material technologies, including e.g. solar cells, transistors, and quantum materials.

The ideal ALD scheme is based on the self-limiting adsorption and reaction of two gaseous precursors with a substrate, in a sequential manner. The exposure of the substrate leads to the formation of not more than a monolayer. This is the origin of the excellent thickness control of ALD. However, despite its importance, particularly for the deposition of high-κ dielectrics, ALD still suffers from unknown surface reaction mechanisms and kinetics. The postulated ideal reaction path, based on a ligand exchanged model, and the passive role of the substrate needs to be revisited.

This study presents new insight into the ALD of HfO_2 on InAs(100) from TDMAHf and water obtained by in situ ambient pressure XPS (APXPS). InAs is an optimal material for the generation of future high-speed MOS due to its higher electron mobility and smaller band gap as compared to silicon. However, the high defect density at the interface between the semiconductor and its native oxide surface has impacted the usability of InAs in MOSFET devices. The ALD of Al_2O_3 and HfO_2 on III-V semiconductors, however, helps to improve the performance of InAs significantly due to the self-cleaning effect that occurs during the early stage of ALD. From APXPS we found that the unwanted oxide despite its thickness is entirely substituted by the desired high-κ oxide already in the first ALD half-cycle, where the high-κ oxide layer is limited to one monolayer. The reaction stops once all oxygen is consumed. The interface between the InAs bulk and the Hf oxide is composed of In-O-Hf. The formation reaction proceeds in the absence of surface hydroxyls, i.e. not according to the hydroxyl-based standard ligand exchange model. Instead, a bimolecular β-hydride elimination reaction is found to lead to the formation of methyl methylene imine. Furthermore, we will present detailed dynamics of the initial surface reactions which cannot be correctly described by the standard ALD model. Time-resolved ambient pressure XPS closes an important gap through its ability to monitor the ALD chemistry while it is ongoing.

SS-Contributed On Demand-136 The Roles of Subsurface Hydrogen and Adsorption of Water on Ni(111), ***Maxwell Gillum**, M. Turano, E. Jamka, D. Killelea,* Loyola University Chicago

Gas-phase H atoms readily absorb into interstitial sites on Ni(111) at temperatures below 140 K, leaving a H-saturated surface.The surface adsorbed H may be removed using collision-induced recombinative desorption.I will present preliminary results demonstrating the ability to prepare clean Ni(111) surfaces loaded with subsurface D atoms.We will use these surfaces to investigate isotope exchange between adsorbed water and the subsurface D(H) atoms.I will also study how the presence of small amounts of adsorbed oxygen atoms on the Ni surface influence isotope exchange.These results will shed light on how subsurface species can influence surface-mediated reactions.

SS-Contributed On Demand-139 Oxidation of Sn at the Cluster-Support Interface: Sn and Pt-Sn Clusters on TiO_2(110), ***Sumit Beniwal**,* University of South Carolina*; W. Chai,* University of Texas at Austin*; K. Metavaryuth, T. Maddumapatabandi, D. Shakya,* University of South Carolina*; G. Henkelman,* University of Texas at Austin*; D. Chen,* University of South Carolina

The growth of Sn and Pt-Sn clusters on TiO_2(110) has been studied by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and density functional theory (DFT).At low Sn coverages (0.02 ML), single-layer high clusters of SnO_x are formed with a narrow size distribution and uniform spatial distribution.XPS experiments indicate that these clusters consist of oxidized Sn, and a corresponding reduction of the TiO_2 substrate is observed.At higher Sn coverages, the surface is still dominated by two-dimensional clusters of SnO_x, but larger three-dimensional clusters of metallic Sn also appear.As the Sn coverage is increased, the number of three-dimensional clusters increases, and the ratio of Sn:SnO_x increases, suggesting that SnO_x and reduced TiO_x form at the cluster-support interface. When Pt is deposited on top of the Sn/SnO_x clusters, the relatively mobile Pt atoms diffuse on the surface and become incorporated into existing Sn/SnO_x clusters.Furthermore, the addition of Pt to the Sn/SnO_x clusters causes the reduction of SnO_x to metallic Sn and the oxidation of Ti^{3+} to Ti^{4+}; this behavior is attributed to the formation of Pt-Sn alloy clusters, which results in the diffusion of Sn away from the interface with the TiO_2 support.In contrast, when Sn is deposited on an equal coverage of Pt clusters, new Sn/SnO_x clusters are formed that coexist with Pt-Sn clusters.However, the surfaces of both Pt on Sn and Sn on Pt clusters are Sn-rich due to the lower surface free energy of Sn compared to Pt.DFT calculations demonstrate that M-TiO_2 bonding is favored over M-M bonding for M=Sn, unlike for transition metals such as M=Pt, Au, Ni, and Co.Furthermore, the substantial charge transfer from Sn to TiO_2 leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late transition metals.DFT studies also confirm that addition of Pt to a Sn cluster results in strong Pt-Sn bond formation and diminished Sn-O interactions.

SS-Contributed On Demand-142 Excited State Relaxation Dynamics in HOPG Using Pump-Probe Momentum Microscopy in the Perturbative Limit, ***Sergii Chernov**, J. Bakalis, A. Kunin, C. Corder, P. Zhao,* Stony Brook University*; M. White,* Brookhaven National Laboratory*; G. Schönhense,* Johannes Gutenberg-Universität Mainz, Germany*; T. Allison,* Stony Brook University

Angle-resolved photoemission spectroscopy (ARPES) has proven to be one of the most powerful techniques for ground state electronic structure studies. Abilities to directly visualize the electron E-vs-$k_\parallel$ distributions, access to the spin degree of freedom[1] and other photoemission effects[2] often make ARPES the method of choice for material electronic properties and crystal structure investigations. Modern ultrafast lasers utilizing high-order harmonic generation (HHG) further enable time-resolved ARPES (TR-ARPES) capable of probing short-lived excited electronic states and their dynamics via pump-probe experiments. However, most HHG-based ARPES systems suffer from relatively low pulse repetition rates. This severely limits the range of experiments that can be conducted and the parameter space that can be explored in TR-ARPES experiments in complex materials.

In order to overcome the aforementioned problems,we combine two state-of-the-art approaches: a high repetition rate HHGXUV generation[3]and Time-of-Flightmomentum microscopy[4]. The XUVsource operating at 61.3 MHz enables experiments at low pump fluences and substantially mitigates the space charge problem. The momentum microscope at the given ~16 ns periodallows to collect simultaneously electron distributionswithin the full Brillouin zone (BZ)andenergy intervalsof up to 3 eV with ~50 meV resolution. Finally, the tight XUV beam focus of less than 30 µm FWHM and further sample region selection with the field aperture of the momentum microscope apertures allow for pump-probe micro-ARPES experiments in perturbative limit with pump pulse energiesdown to nJ/cm^{2}scales.

We will presentan example study on graphiteusing 515 nm (2.41 eV) *p*-and *s*-polarized pump light. Measurements were performed with different probe energies, i.e. different $k_\perp$ cuts of the BZ across H and K points. A range of pump fluences from 1 to 100 µJ/cm^{2}wereexplored to ensure non-perturbative excitation character.The full BZ data accumulated allows the extraction of fundamental electron-phonon and electron-electron scattering processes with unprecedented detail.

SS-Contributed On Demand-145 C-H Bond Dissociation of Methane on Rh(111): Remarkable Activity of Step Sites, ***Xingyu Wang**, I. Harrison,* University of Virginia

Steam reforming is one of the most important industrial chemical processes. However, it is usually performed in large-scale reactors and has high energy demand. Catalytic partial oxidation of methane, on the other hand, can be carried out in compact and low capital-cost reactors to produce syngas. Rh is generally considered the best metal catalyst for partial oxidation.

We studied the initial C-H bond cleavage of methane under non-equilibrium conditions on Rh(111), where the temperature of the impinging gas molecules could be different from the surface temperature, and the angle of incidence of the impinging molecules could be varied. This was realized in an ultra-high vacuum chamber with a heated effusive molecular beam doser, which generates a beam of molecules with a cosine angular distribution and energy distributions fully thermalized to the doser temperature. The surface temperature of the Rh(111) crystal could be controlled independently and carbon deposited on the surface was measured by Auger electron spectroscopy, which allowed dissociative sticking coefficients to be determined.

Using a precursor mediated microcanonical trapping model, molecular translational energy directed along the surface normal was found to be about twice as effective as vibrational energy in promoting the reactivity of methane. Unlike on the Pt (111) surface where (111) terrace site reactivity dominates, methane reactivity on Rh (111) indicates that Rh step sites are not easily poisoned by C accumulation and can contribute substantially to the overall methane reactivity, especially at lower temperatures. Such multidimensional reactivity studies allow for relatively facile designation of the terrace and step activity which allows us to reconcile single crystal and Rh foil reactivity studies.

Surface Science Division

Room On Demand - Session SS-Invited On Demand

Surface Science Invited On Demand Session

SS-Invited On Demand-1 Halide Ion Mobility in Metal Halide Perovskites and its Impact on Photovoltaic Performance*, Prashant Kamat,* University of Notre Dame **INVITED**

The intrinsic ionic defects, specifically halide ion vacancies, often dictate the mobility of halide species within the perovskite film during the operation of solar cells.Of particular interest is the halide ion mobility in metal halide perovskites, which plays an important role in determining the performance of perovskite solar cells. Photoinduced phase segregation seen in mixed halide perovskite films under steady state irradiation offers a convenient way to visualize halide ion segregation. Interestingly, upon storage in dark, the process is reversed and the original mixed halide composition gets restored. Whereas entropy of mixing explains the thermally activated mixing of halide ions to yield mixed halide perovskite, the opposite trend observed during photoirradiation remains an intriguing phenomenon.The threshold energy of incident light to observe halide segregation increases with increasing temperature. The diffusion of these halide species, which is tracked through changes in the absorption spectra at different temperatures, offers a direct measurement of thermally activated halide diffusion in perovskite films. The thermally activated halide exchange shows the challenges of employing layers of different metal halide perovskites in stable tandem solar cells.

SS-Invited On Demand-7 Chemistry and Hydrogen Bonding Environment at Environmental Surfaces as Seen by X-ray Photoelectron and Electron Yield NEXAFS Spectroscopies*, Markus Ammann,* Paul Scherrer Institut, Switzerland **INVITED**

X-ray photoelectron spectroscopy (XPS) of typically core atomic electronic levels provides chemical composition information and electron yield near edge X-ray absorption fine structure (NEXAFS) spectroscopy gives insight into the structure of the local molecular environment. The low inelastic mean free path of electrons of a few nanometer enables sensitivity for the condensed matter – gas interfacial region. The development of ambient pressure electron analyzers has offered tremendous opportunities for molecular understanding of environmentally relevant aqueous solution surfaces, ice surfaces, and mineral oxides, all in presence or absence of reactive trace gases and in or out of equilibrium with water vapor. Applications involving the characterization of interfacial structure at mineral oxides and ice, the protonation state of acids or the direct observation of reaction intermediates at the surface of liquid water will be presented.

SS-Invited On Demand-13 Thin Film Growth One Step at a Time: Unraveling Mechanisms in Atomic Layer Deposition*, Stacey Bent,* Stanford University **INVITED**

With the growing interest in functional nanoscale materials for applications such as electronics, catalysts, and batteries, methods for fabricating materials with atomic-level control are becoming increasingly important. Atomic layer deposition (ALD) is a vapor-based method that provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformality, thickness control at the Angstrom level, and tunable film composition. This talk will describe research into the fundamental processes that drive ALD. Two ALD systems will be presented in which a combination of characterization methods is applied to elucidate nucleation and growth mechanisms. In the first system, ALD of binary and ternary metal oxides using ozone as a counterreactant show unusual behavior implicating the importance of trapped reactive oxygen species in these ALD processes. For example, in the growth of ternary Ni-Al-O films using supercycles of nickel oxide and aluminum oxide ALD, Al uptake is greatly enhanced when Al_2O_3 ALD followed a NiO ALD cycle, a result that may arise from the presence of nickel superoxide species after ozone exposure. In ALD of iron oxide by t-butylferrocene and ozone, growth per cycle of greater than one monolayer of Fe_2O_3 per cycle is observed and explained by the presence of excess oxygen stored in the surface regions of deposited films. In the second system, ALD of MoS_2 thin films as well as ALD of metal oxides on MoS_2 will be described. We show that the concentration and size of ZnO nanocrystals grown on MoS_2 by ALD can be independently tuned by controlling the growth conditions. We also introduce a kinetically-driven ALD process for growing stoichiometrically controlled, crystalline MoS_2 from $Mo(CO)_6$ and H_2S at temperatures as low as 190 °C. Insights into the effect of ALD process conditions on growth behavior and materials properties will be presented.

SS-Invited On Demand-19 Interaction of Small Heteroatomic Organic Compounds with Ceria*, Ye Xu,* Louisiana State University **INVITED**

Ceria is an abundant and versatile technological material owing to its ability to readily change between oxidation states and store, release, and conduct oxygen.Its surfaces present regular arrays of acidic, electrophilic Ce cations ($Ce^{\delta+}$) and basic, nucleophilic O anions ($O^{\delta-}$) in close proximity, accessible to different extents depending on the crystalline facet and degree of surface reduction.Because of the amphoteric nature of its surfaces, ceria can interact strongly with a variety of Brønsted/Lewis acid/base compounds, oxo compounds (molecules derived from oxoacids such as aldehydes, ketones, esters and phosphates), and their heteroatomic counterparts.I will present the findings of our theoretical investigation into the adsorption of several such organic compounds and their reactivity on ceria in terms of energetic, geometric, electronic, and vibrational properties.Reactivity patterns that make this oxide potentially useful for catalyzing a broad range of organic reactions under mild conditions will be discussed.

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