Plasma Science and Technology Division
Room 104A - Session PS+AS+EM+SS-MoM

Plasma-Surface Interactions

Moderator: Yohei Ishii, Hitachi High Technologies America Inc.

8:20am **PS+AS+EM+SS-MoM1 Atomic-scale Numerical Simulation of a Nanometer-Scale Hole Etching of SiO2 with a Carbon Mask**, ***Charisse Marie Cagomoc***, *M. Isobe, S. Hamaguchi,* Osaka University, Japan

The current generation of mass-produced semiconductor devices uses nanometer-scale technologies to fit millions of transistors in a single chip. However, the demand for higher integration density is still increasing. For example, sub-10 nanometer transistors have been already established for experimental devices, and fabrication technologies of such devices for mass production are now being developed. For nanometer-scale fabrication processes, the granularity of the structure reflecting the finiteness of atomic sizes and the stochasticity of atomic motion may play important roles in determining the final structure. In this study, to understand such atomic-scale effects in nano-scale fabrication processes, we performed molecular dynamics (MD) simulations of etching processes for silicon dioxide (SiO_2) with a carbon mask having a 4-nm diameter hole by energetic fluorocarbon ions. The incident ion energy was typically in the range from 200eV to 1000eV. For example, in the case of CF_3+ ion injections, we observed that the depth of the etched out SiO_2 increased with increasing incident ion energy while the channel width became narrower as the etching of SiO_2 went deeper. Tapering of the carbon mask was also observed when the incident ions hit and deform the mask instead of going straight towards the SiO2. Furthermore, if the incident energy was too high (e.g., 1000 eV in this case), closing of the carbon mask hole occurred due to the formation of long carbon chains that moved across the hole and were bonded to the opposite side. Deposition of carbon atoms from the mask onto the sidewalls of the etched SiO_2 was also observed, which caused the formation of silicon carbide and may have impeded horizontal etching of SiO_2.

8:40am **PS+AS+EM+SS-MoM2 SF_6/O_2 Plasma Nanotexturing of Silicon: Decoupling How Ion Flux and Ion Energy Matter**, ***Guillaume Fischer***[1], Institut Photovoltaïque d'Ile-de-France (IPVF), France; *E. DRAHI, S.A. FILONOVICH,* Total SA Renewables, France; *E.V. Johnson,* LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, France

Crystalline silicon (c-Si) solar cell performance can be improved by reducing front surface reflectance. A drastic decrease may be obtained by texturing the surface at the nanoscale ("nanotexturing"), leading to a graded refractive index from air to c-Si. SF_6/O_2 plasma etching of c-Si in a capacitively coupled radiofrequency (CCP-RF) discharge is known to induce spontaneous nanotexturing. This phenomenon – typically resulting in the formation of conical nanostructures (NS) with typical sizes ranging from 30 to 500 nm – occurs through *in-situ* formation of non-volatile inhibitors on the surface. The latter compete with simultaneous physical and chemical etching, and all these mechanisms may be influenced by ion bombardment.

In the present study, the ion energy distribution at the substrate electrode is tuned using Tailored Voltage Waveforms (TVWs) excitation in a reactive ion etching system. TVWs are obtained by adding harmonic frequencies with controlled amplitudes and phase-shifts to the basis driving signal at 13.56 MHz. This technique may give rise to amplitude and slope asymmetries in electronegative plasmas such as the SF_6/O_2 mixture.

Taking advantage of the edge-high total ion flux radial profile on the electrode but with a uniform energy distribution profile, we investigate the influence of both ion energy and ion flux on the nanotexturing process. Process conditions (etching time and driving voltage, i.e. sinusoidal signal or TVWs) are varied, and four samples are simultaneously textured for each set of conditions. The variations in etch rate suggest an ion energy-dependent etching yield. A phenomenological model (etching yield varying with the square root of the ion energy above a threshold at 13 eV) is proposed, and leads to the determination of a clear dependence between the energy weighted ion fluence and the final total hemispherical reflectance of the samples.

This trend is of great relevance for photovoltaic applications, and is explained by the constant increase in NS height during the process, which gradually smoothens the transition of refractive index from air to c-Si. However, the instantaneous ion flux is still observed to influence the aspect ratio (ratio between average height and width of the NS): the higher the ion flux, the higher the aspect ratio. This effect may stem from reduced lateral expansion of inhibitor species on the NS flanks due to the higher ion flux, and will affect the subsequent surface passivation required for photovoltaic applications. Finally, design rules for silicon nanotexturing using SF_6/O_2 plasma are drawn from the observed trends.

9:00am **PS+AS+EM+SS-MoM3 Corrosion Resistance to F and Cl plasma of Yttrium Oxyfluoride (YOF) formed by Sintering**, ***Akinobu Teramoto***, *Y. Shiba, T. Goto,* Tohoku University, Japan; *Y. Kishi,* Nippon Yttrium Co., Ltd, Japan; *S. Sugawa,* Tohoku University, Japan

Corrosion resistance to the reactive species in some kinds of plasma is very important to construct the reliable semiconductor process equipment. Especially the Fluorine and/or Chlorine plasma have the strong corrosiveness, and then it is strongly required that the inner wall material of the plasma chamber and the components in the plasma chamber have corrosion resistance to them. We have reported the Yttrium oxyfluoride (YOF, Y:O:F=1:1:1) film has the higher resistance to some plasma conditions (N_2/Ar, H_2/Ar, NH_3/Ar, NF_3/Ar, O_2/Ar) than the Y_2O_3 and YF_3 films [1, 2]. In this presentation, we report the corrosion resistance to NF_3/Ar, Cl_2/Ar and O_2/Ar plasma of YOF formed by sintering. The Y, O and F composition was controlled by mixing ratio of the YOF, YF_3, and $Y_5O_4F_7$ before the sintering, as the results, the O concentration was varied from 3 to 12 %. All YOF formed by the sintering are more stable to NF_3/Ar and O_2/Ar plasma than the YOF film and both Y_2O_3 film and formed by sintering. Cl_2/Ar plasma shows the stronger corrosion effect to the Y_2O_3 and YOF's, however the corrosion resistance to Cl plasma of YOF's is higher than the Y_2O_3.

These results indicate that the YOF is much stable against the corrosion by the plasma, and YOF formed by sintering is the promising material to construct the components in the plasma chamber.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

References

1. Y. Shiba, A. Teramoto, T. Goto, Y. Kishi, Y. Shirai and S. Sugawa, J. Vac. Sci. Technol. A, **35** (2), 021405 (2017).

2. Y. Shiba, A. Teramoto, T. Goto and Y. Kishi, p. 111, AVS 64th International Symp., Tampa, 2017.

9:20am **PS+AS+EM+SS-MoM4 Decay of Hydrogen in NF_3/Ar and O_2/Ar Cleaning Process by Optical Emission Spectroscopy**, ***Hanyang Li***, *Y. Zhou, V.M. Donnelly,* University of Houston; *J. Chiu, X. Chen,* MKS

Fluorine atom-generating plasmas are commonly used in many cleaning processes after chambers have been exposed to a variety of etching and deposition reactants and products. The most common feed gas used in these applications is NF_3, due mainly to its ease of dissociation. Repeated processing and chamber cleaning cycles can cause changes in the plasma source, thought to be due mainly to an altering of the nature of the chamber wall protective coatings. In the present study, high power density (5 – 50 W/cm^3), low frequency (400 kHz) toroidal inductive plasmas were operated with H_2/Ar (4/96) and N_2/H_2/Ar (3/9/88) feed gases for various periods, alternating with exposure to NF_3/Ar, O_2/Ar, or pure Ar "chamber cleaning" plasmas. H Balmer-alpha optical emission intensity, ratioed to emission from Ar at 750.4 nm, was measured during H_2/Ar exposure and the following cleaning plasma. Hydrogen was detected evolving from the anodized Al plasma source wall coating. The decay of intensity ratio of H/Ar increased with increasing H_2/Ar plasma exposure. NF_3/Ar plasmas enhanced evolution of H, tentatively ascribed to diffusion of F into anodized Al (most likely as F^-), which reacts with H that would otherwise remain trapped in the layer. The HF product then out-diffuses, leading to plasma dissociation and H emission. Conversely, O_2/Ar plasmas suppressed the evolution of H, presumably because O bonds to Al in anodized Al and ties up hydrogen as bound OH.

9:40am **PS+AS+EM+SS-MoM5 Plasma-surface Interactions in the Strongly Coupled Regime**, ***Thomas Morgan***, DIFFER, Netherlands **INVITED**

At high fluxes and densities the interaction of a plasma with the walls of its confinement enter the strongly coupled regime [1], where the mean free paths for collisional processes become much smaller than those of the plasma scale size. The surface morphology in such cases may be pushed far out of equilibrium and in turn the recycling and erosion strongly perturbs the near-surface plasma. Such conditions are reached in high flux plasma processing as well as the exhaust region of future large-scale fusion reactors such as ITER and DEMO. The linear plasma generator Magnum-PSI

---

[1] **Coburn & Winters Student Award Finalist**

[2] is uniquely capable of achieving high density low temperature plasmas with high similarity to fusion reactor exhaust fluxes. Using this device the power handling, long term erosion and evolution of plasma facing materials for ITER and DEMO can be studied, as well as the self-organisation effects and novel structures which occur under such conditions. At plasma-liquid metal interfaces considered as advanced wall components this strong coupling can give rise to vapour shielding of the surface, indicating a novel method to limit heat loading damage to wall surfaces in the reactor exhaust [3]. An overview of results will be given showing how this device is addressing urgent questions for ITER, helping to develop advanced walls for DEMO and beyond, and exploiting non-equilibrium for plasma processing.

[1] A.W. Kleyn et al. Phys. Chem. Chem. Phys. 8 (2006) 1761–1774

[2] G. De Temmerman et al. Fusion Eng. Des. 88 (2013) 483-487

[3] G.G. van Eden et al. Phys. Rev. Lett. 116 (2016) 135002

10:40am **PS+AS+EM+SS-MoM8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing**, ***Angela Hanna***[1], *E.R. Fisher,* Colorado State University

Zeolites have been widely used for adsorption, catalysis, and gas separation processes. Despite their extensive use, the ability to control the surface properties of zeolites remains unoptimized. Plasma modification presents an ideal modification methodology with a wide parameter range and the potential to create tailored surface properties and functionalities. Thus, we sought to improve material performance through plasma surface modification, as well as through fabrication of various zeolite constructs (i.e., native zeolites, pellets and electrospun fibers). Moreover, our approach to understand the fundamental plasma chemistry allows us to provide significant insight into mechanisms that will ultimately provide a more thorough evaluation of plasma processing for zeolite surface modification. We employed a range of characterization tools to assess materials before and after plasma treatment and optical spectroscopies to examine the gas-phase of the plasma, both with and without zeolites to evaluate the impact of the material on the gas-phase. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and powder X-ray diffraction were utilized to assess surface chemistry, substrate morphology, and bulk characteristics of the material, respectively, before and after plasma exposure. Water contact goniometry was employed to evaluate the surface wettability, where untreated zeolites were nominally hydrophilic. Here, we explored two fluorocarbon (FC) precursors (i.e., C_2F_6 and C_3F_8) to create more hydrophobic surfaces than the untreated materials. XPS analysis reveals surface fluorination and/or formation of a FC coating on the material. $H_2O_{(v)}$ plasmas were also employed to create a more hydrophilic zeolite surface, while maintaining a porous, interconnected network. By also studying the gas-phase, we can glean how the material changes the plasma environment. Species interactions and plasma energetics are intertwined; thus, temporally-resolved data are necessary to accurately probe the intricate dynamics within plasmas. We have investigated formation and destruction mechanisms of key excited state species (i.e., CF, CF_2, OH) to provide mechanistic insight that could be correlated with system energetics data and material properties. Emission spectroscopy was also used to measure the relative gas phase densities of the aforementioned key species as a function of plasma operating parameters (i.e., power, gas mixture, substrate architecture). Our studies have revealed correlations between gas-phase spectroscopic analyses, the gas-surface interface, and the resulting plasma modified surface properties, ultimately leading to improved plasma processes.

11:00am **PS+AS+EM+SS-MoM9 Generation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials**, ***Shota Nunomura***, *I. Sakata, K. Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In state-of-the art semiconductor devices, electronic defects strongly influence the device performance. The electronic defects are often generated during the device fabrication, where a variety of plasma processing technology is used for film deposition, gate etching, dopant implantation and so on. Most defects are recovered by post-annealing, however some defects remain in the devices. Because these defects usually deteriorate the device performance, reduction of these defects is required. However, the kinetics of generation and annihilation of the defects are not fully understood yet.

We studied the kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H) during H_2 and Ar plasma treatments. The generation and annihilation of defects are monitored via in-situ photocurrent measurement during the treatment [1-2]. A decrease in the photocurrent indicates the generation of defects whereas an increase in the photocurrent indicates the annihilation of defects. This photocurrent-based monitoring is highly sensitive in the detection of small amount of defect density (~10^{16}cm^{-3}).

The photocurrents in a-Si:H films under various conditions of H_2 and Ar plasma were measured. From the measurements, we find the following [3]. (i) Each plasma treatment immediately causes the generation of defects, indicated by a strong reduction in the photocurrent. (ii) The defects are generated dominantly by the radicals such as hydrogen atoms (H) and argon metastable atoms (Ar^*). (iii) The residual defects are created by the bombardment of Ar^+ ions rather than H_3^+ ions, radicals and photons. However, the residual defects are recovered mostly by an additional H_2 plasma and post-annealing treatment. (iv) The radicals and photons also generates defects, however these defects are annihilated by the simple post-annealing. The details of the experimental setup, results and discussion are given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

[1] S. Nunomura, I. Sakata, and M. Kondo,*Appl. Phys. Express* **6**, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014). [3] S. Nunomura et al., submitted.

11:20am **PS+AS+EM+SS-MoM10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure**, ***Adam Pranda***, *S.A. Gutierrez Razo, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Fluorocarbon-based plasma chemistry is an integral component in enabling the pattern transfer step in the semiconductor manufacturing process. Although significant work has gone towards understand the overall etching behavior, surface roughness, and chemistry development for continuous-wave (CW) plasmas with Ar/fluorocarbon admixtures,[1] a complete understanding of the photoresist layer structure evolution and surface roughness distribution has not been well established. Specifically, under high-energy ion bombardment, a dense amorphous carbon (DAC) layer forms at the surface, impacting the etch resistance and surface roughness. For discrete evaluation of the DAC layer/fluorocarbon interaction, we employed a pulsed plasma setup in which a biased, steady-state Ar plasma was used to develop DAC layers of various thicknesses at the photoresist surface, after which fluorocarbon (C_4F_8) pulses of various lengths were introduced. We sought to answer three key questions: 1. How does the fluorocarbon interaction with the DAC layer impact the layer structure? 2. How is the surface roughness affected by the fluorocarbon interaction? 3. How does the pulsed process compare to a CW Ar/C_4F_8 admixture process?

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and X-ray photoelectron spectroscopy at various points during the plasma exposure on an industry-standard 193 nm photoresist, several model polymers, and a 3-color-lithography-compatible photoresist that we are developing. Atomic force microscopy (AFM) was used to monitor the surface roughness evolution and the distribution was calculated using a power spectral density (PSD) analysis.

From the combined analyses, we find that the fluorocarbon depletes the DAC layer by a partial conversion of the surface of the DAC layer into an F-rich mixed layer. Furthermore, the mixing of the fluorocarbon into the DAC layer results in an overall smoothening of the sample surface. By comparing the pulsed process to the CW process, we evaluate the significance of the layer structure in determining the surface behavior in response to variations in fundamental plasma parameters such as the ion energy or exposure time.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

[1] S. Engelmann et al., J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. **27**, 1165 (2009).

---

[1] **National Student Award Finalist**

11:40am **PS+AS+EM+SS-MoM11 Fundamental Studies of Plasma Species with Organic Materials of Varying Hydrogen and Oxygen Composition by Computational and Experimental Approaches***, **Yusuke Fukunaga**,* Nagoya University, Japan*; P.L.G. Ventzek, B. Lane,* Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center America, LLC*; M. Sekine, T. Tsutsumi, H. Kondo, K. Ishikawa,* Plasma Nanotechnology Research Center, Japan*; R. Upadhyay,* Esgee Technologies*; L. L. Raja,* The University of Texas at Austin*; G. Hartmann,* McKetta Department of Chemical Engineering, The University of Texas at Austin*; G. S. Hwang,* The University of Texas at Austin*; M. Hori,* Institute of innovation for future society, Japan

Organic film etching is important for semiconductor device fabrication especially as it relates to self-aligned-multiple-patterning in which sub-nanometer scale pattern replication is critical. Even though the etching of organic materials has been studied for decades (e.g., O_2 plasma ashing), new process applications (e.g. ALE) and new chemistry regimes render older models of organic etching such as those employing the Ohnishi parameter of limited use.[1] Existing kinetic models rely on untested assumptions such as the role of dangling bonds as reaction initiating sites.[2] A need exists to revisit the fundamentals of plasma surface interactions as they pertain to the etching of organic films. Moreover, a need exists to incorporate fundamental kinetic models with macroscale models which could be used for process development.

Progress has been slow because of the computational weight of modeling the chemical kinetics and difficulty defining a tractable problem. In this presentation, we describe the use of an integrated modeling framework involving fundamentals-based ab-initio and plasma chemistry simulations with high performance computing to describe chemical kinetics on model polymer systems. In O_2 and Ar plasmas, we use finite carbon size strands with varying degrees of O, OH or H termination as model structures. For simplicity, the structures are polyethylene-like. We use density functional theory (DFT) to model the interactions between plasma species and representative structures. To estimate the relative importance of plasma species and their energy, we derive species and energy flux from a macroscale plasma chemistry model. Both DFT and ab-initio molecular dynamics (AIMD) simulations are used to probe the chemical stability of representative structures to different plasma species (e.g., Ar, O) and energy fluxes. We found that O addition to H terminated structures results in OH group formation on polyethylene by exothermic reaction. Ar ion bombardment formed carbon strands may also be oxidized. The resultant structures (oxo-carbon) are also stable up to large oxygen to carbon ratios. The stability to Ar ion bombardment will be presented. An essential test of any new mechanism is experimental validation. In addition to the computational results, we will present experimental results ranging from basic etch rate measurements to measurements of plasma processed material chemical composition (e.g., XPS).[3]

References:

[1] H. Gokan, *et al.*, J. Electrochem. Soc.: Solid-state Sci. Technol. **130**, No. 1, 143 (1983).

[2] F. D. Egitto, Pure & Appl. Chem. **62**, No. 9, 1699 (1990).

[3] D. U. B. Aussems, *et al.*, Chem. Sci. **8**, 7160 (2017).

Surface Science Division
Room 203C - Session SS+HC+MI-MoM

Dynamical Processes at Surfaces

Moderator: Gareth Parkinson, TU Wien

8:20am **SS+HC+MI-MoM1 Light Induced Single-Molecule Dynamics at Surfaces***, **Wilson Ho**,* University of California, Irvine **INVITED**

Inhomogeneity of different length scales is one of the fundamental characters of matter that has its origin in the spatial variations of the charge and mass distributions. While many changes in nature and in the laboratory can be observed with the naked eyes, ultimately the interactions that lead to these changes occur at the atomic scale. In addition, heterogeneity influences the time scale that transformations occur at different locations, and the average time may differ significantly from the local times. The desire to understand and control changes in the charge and mass distributions would require experimental tools that possess simultaneous spatial and temporal resolutions to reveal the heterogeneity. This joint Å-fs resolution can be achieved by the combination of a femtosecond laser with a low temperature scanning tunneling microscope (fs-STM) that probes chemical transformations of single molecules. These experiments demonstrate the fs-STM approach in probing the effects of heterogeneity in space and time on the chemical dynamics in single molecules.

9:00am **SS+HC+MI-MoM3 Probing the Effects of Surface Structure on the Dissociative Chemisorption of Methane***, **Eric High**[1], D.G. Tinney, A.L. Utz,* Tufts University

Vibrational state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Insights into energy flow during reaction obtained from observations of non-statistical mode-specific and bond-selective enhancements observed for methane and it's isotopologues on transition metal surfaces are one example. By providing reactive gas-molecules with precisely defined energy in well-defined energetic coordinates, state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. In this work, we will present vibrational state-resolved data collected via IR laser excitation of the antisymmetric stretch of supersonically expanded CH_4 gas molecules incident on a Ni(997) surface. We will focus on measurements investigating both the low and high incident energy regimes on this lightly stepped single crystal at a wide range of surface temperatures (T_S = 120 K to 1000 K). We will explore the possibility of benchmarking site-specific reaction barriers for dissociative chemisorption with molecules near the energy threshold for reaction. For higher energy molecular beams incident on higher surface temperatures, we will report on how the presence of steps on the Ni(997) surface modifies the kinetics of surface-bound C diffusion into the Ni subsurface and bulk and how this process impacts subsequent methane reactivity on this surface.

9:20am **SS+HC+MI-MoM4 Adsorption and Diffusion of NH_3 on Anatase-TiO_2 (101)***, **Kræn Christoffer Adamsen**, S. Koust, E.L. Kolsbjerg, B. Hammer, S. Wendt, J.V. Lauritsen,* Aarhus University, Denmark

Fundamental understanding of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on VO_x/TiO_2 based catalysts , and adsorption of ammonia on such oxides is therefore of great importance for fundamental understanding of NO_x-removal and SCR catalysis. Here we present a fundamental study of the static and dynamic behaviour of ammonia on anatase-TiO_2 (101), the predominant facet on anatase-TiO_2 nanoparticles. High resolution Scanning Tunnelling Microscopy (STM) of static adsorbed ammonia molecules at room temperature, indicates a strong binding to the surface. Through synchrotron radiation XPS ammonia was found to adsorb molecularly. The strong binding of ammonia was further quantified by Temperature Programmed Desorption (TPD) which also shows a highly coverage dependent binding energy, indicating molecular repulsion. All experimental obtained results are in accordance with a proposed theoretically calculated DFT-model of ammonia absorption.

Next, single ammonia molecule diffusion measured utilizing the high-speed Aarhus STM, show diffusibility to all neighbouring sites. Molecular repulsion also show a clear effect on static structures, where nearest neighbouring site occupation is rarely observed. Statistical analysis of intermolecular coordination supplied repulsion energies, which agree with observed values in TPD spectra and theory. For diffusion, we conclude that molecular repulsion increases the diffusibility for higher coordinated ammonia molecules. However when two ammonia occupy two nearest neighbour sites, they have the possibility of diffusing through a rolling effect, where ammonia can move more easily in one direction, this phenomena has also been seen for water on other oxide surfaces. Our analysis thus shows a surprisingly complex diffusion behaviour of NH3 on anatase TiO_2(101), which however resembles water dimer diffusion of water dimers on Rutile-TiO_2 (110).

9:40am **SS+HC+MI-MoM5 Non-equilibrium Growth of Metastable Clusters as a Means of Controlling Supramolecular Structure.***, **Ryan Brown**,* Clarkson University*; A.S.A. Kandel,* University of Notre Dame

This poster will review the use of non-equilibrium growth conditions to produce supramolecular structures not easily accessible using traditional self-assembly approaches. Specifically, the formation of cyclic, hydrogen-bonded clusters at the vacuum-solid interface following the direct injection of a solution into a high vacuum chamber gives insight into the utility of employing non-equilibrium growth conditions for producing supramolecular structures with metastable configurations. When deposited in a rapidly evaporating droplet, hydrogen bonding small molecules can form clusters with 5-fold symmetry if the correct

---

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

combination of hydrogen bonding groups are present. These features persist at room temperature, but evolve into more complex structures upon mild annealing. Initial studies of this phenomenon in ferrocenecarboxylic acid, 1,1'-ferrocenedicarboxylic acid, indole carboxylic acid, and isatin will be discussed. Finally, future systems and directions of study will be discussed.

10:00am **SS+HC+MI-MoM6 Ultrafast Dynamics of Reaction Pathways on Metal Surfaces*, Jerry LaRue,*** Chapman University

Important chemical processes often occur on the femtosecond timescale, requiring the use of femtosecond excitation and probing techniques to study them. Optical femtosecond laser pulses are a convenient method of initiating catalytically important reactions on metal surfaces, such as CO hydrogenation and CO oxidation, on the femtosecond timescale. Using femtosecond x-ray pulses from free electron lasers (FEL), we have selectively probed the bond making and breaking processes of these reactions using O and C k-edge x-ray absorption and emission spectroscopies to obtain time-resolved electronic structure maps. These electronic structure maps reveal the time evolution of different surface species along the reaction pathway, providing new insights into the reaction dynamics on metal catalysis. This talk will highlight past and recent results in reaction dynamics on metal surfaces as investigated using femtosecond x-ray pulses and supported through density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations. Specific systems include CO desorption CO oxidation, and CO hydrogenation on ruthenium.

10:40am **SS+HC+MI-MoM8 Designer Solids via Multi-Heteroepitaxy: Layer-by-Layer Deposition of Molecular Frameworks on Solid Substrates*, Christof Wöll,*** Karlsruhe Institute of Technology, Germany **INVITED**

Realizing molecular “Designer Solids” by programmed assembly of building units taken form libraries is a very appealing objective. Recently metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical [1,2], photoelectro-chemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [8]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical [9] and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Furthermore, we will discuss further applications realized by loading MOFs with nanoparticles or quantum dots.

References:

[1] A. Dragässer, O. Shekhah, O. Zybaylo, C. Shen, M. Buck, Ch. Wöll, D. Schlettwein

Chem. Comm., 48, 663 (2012)

[2] J. Liu, M. Paradinas, L. Heinke, M. Buck, C. Ocal, V. Mugnaini, Ch. Wöll

Chem.Electro.Chem., 3, 713 (2016)

[3] Lu Ye, J. Liu, Y. Gao, Ch. Gong, M. Addicoat, Th. Heine, Ch. Wöll, L. Sun

J. Mater. Chem. A, 4, 15320, (2016)

[4] J. Liu, W. Zhou, J. Liu, I. Howard, G. Kilibarda, S. Schlabach, D. Coupry, M. Addicoat, S. Yoneda, Y. Tsutsui, T. Sakurai, S. Seki, Zh. Wang, P. Lindemann, E. Redel, Th. Heine, Ch. Wöll, Angew. Chemie Intl. Ed., 54, 7441 (2015)

[5] J. Liu, W. Zhou, J. Liu, Y. Fujimori, T. Higashino, H. Imahori, X. Jiang, J. Zhao, T. Sakurai, Y. Hattori, W. Matsuda, Shu Seki, S. K. Garlapati, S. Dasgupta, E. Redel, L. Sun, Ch. Wöll, Journal of Mat. Chem. A, 4, 12739 (2016)

[6] M. Oldenburg, A. Turshatov, D. Busko, S. Wollgarten, M. Adams, N. Baroni, A. Welle, E. Redel, Ch. Wöll, B. S. Richards, I. A. Howard, Adv. Mater., 28, 8477 (2016)

[7] Z. Wang, A. Blaszczyk, O.Fuhr, S.Heissler, C.Wöll, M.Mayor, Nat. Comm., 8, 14442 (2017)

[8] j. Liu, C. Wöll, Chem. Soc. Rev. 46, 5730-5770 (2017)

[9] J. Liu, T. Wächter, A. Irmler, P.G. Weidler, H. Gliemann, F. Pauly, V. Mugnaini, M. Zharnikov, Ch. Wöll, ACS Applied Materials & Interfaces, 7, 9824, (2015)

11:20am **SS+HC+MI-MoM10 Isotope Enrichment via Non-Equilibrium Differential Condensation and Reflection using Supersonic Beam Gas-Surface Scattering*, Jacob Graham,*** *A. McMillan, K. Nihill, S.J. Sibener,* University of Chicago

Isotopically enriched materials have a variety of uses including chemical labeling, energy, medicine, and quantum computing. To stimulate the further development of these applications, modern, efficient isotope enrichment methods are needed. Non-equilibrium supersonic beam gas-surface scattering and differential condensation is shown to be a new and broadly applicable route to isotope enrichment. This enrichment is demonstrated with ^{36}Ar and ^{40}Ar isotopes reflecting from low temperature condensates of argon, with differences arising in the condensation coefficient, which depend on the degree of collisional energy exchange for each isotope at the interface. The enrichment factors were found to be tunable as a function of incident beam kinetic energy. For example, ^{36}Ar was found to be *enriched* relative to ^{40}Ar in the scattered fraction by greater than a factor of two, for a seeded beam of argon in helium having incident velocity 1650 m/s. In a separate and complementary experiment under the same conditions, the amorphous argon condensate was found to be *depleted* in its ^{36}Ar content, confirming this effect. This observed isotope selectivity during deposition introduces a new method for isotopic enrichment and purification as well as *in-situ* isotopic materials engineering.

11:40am **SS+HC+MI-MoM11 Structural Reorganization of Sequentially Adsorbed Two-component Self-assembled Monolayers after Soft Ultraviolet Irradiation***, C. Gerber, **Rebecca Quardokus,*** University of Connecticut

Sequentially adsorbed anthracene dicarboxylic acid and octanethiol on Au(111) form ordered regions of octanethiol, gold vacancy islands, and areas of disorder near domain boundaries and vacancy islands. Vapor deposition of octanethiol after drop-cast deposition of anthracene dicarboxylic acid on Au(111) results in small (√3 x √3)R30° and c(4x2) octanethiol domains. Initial exposure to soft ultraviolet irradiation increases disorder with only a few small close-packed octanethiol domains remaining. Repeated exposure to soft ultraviolet irradiation shows some removal of octanethiol molecules and sequential imaging by scanning tunneling microscopy gives snapshots of the stepwise reordering of the domains that ultimately leads to a structurally reordered monolayer consisting of larger domains of low-coverage octanethiol in a *p* x √3 structure.

Tribology Focus Topic
Room 201A - Session TR+AS+NS+SS-MoM

Tribology Focus Session

Moderators: Mehmet Z. Baykara, University of California, Merced, Prathima Nalam, University at Buffalo - SUNY

8:20am **TR+AS+NS+SS-MoM1 Structural Superlubricity: History, Breakthroughs, and Challenges*, Mehmet Z. Baykara,*** University of California, Merced **INVITED**

The idea of *structural superlubricity* holds immense potential for the realization of nearly frictionless sliding in mechanical systems, with implications for fields as diverse as environmental conservation and space travel. The basic principle of structural superlubricity involves the proposition that friction should diminish at an interface formed by atomically-flat and molecularly-clean crystalline surfaces with different lattice parameters and/or incommensurate orientation. Despite the rather straightforward character of its basic principle, the realization of structural superlubricity under ambient conditions has been challenging due to the requirement of molecular cleanliness at the interface.

In this talk, we will first briefly review three decades of structural superlubricity research by emphasizing important milestones and breakthroughs. Subsequently, we will present results of nano-manipulation experiments from our lab, which demonstrate the remarkable occurrence of structural superlubricity for gold and platinum nano-islands sliding on graphite under ambient conditions. Complementary to the experiments, results of *ab initio* calculations will be discussed, which (i) reveal that the noble metal–graphite interface is expected to remain largely free from contaminant molecules, leading to structurally superlubric sliding under ambient conditions, and (ii) confirm the experimental observation of larger friction forces for platinum, attributable to higher energy barriers encountered during sliding. The experiments additionally demonstrate that the scaling power between friction force and contact size is independent of the chemical identity of the sliding atoms, but is determined by the geometric qualities of the interface. The talk will conclude with a review of remaining challenges for structural superlubricity, in particular those involving size- and deformation-related limits.

9:00am **TR+AS+NS+SS-MoM3 An Examination of the Nature of Bonding during Indentation and Sliding using MD and in-situ Nanoindentation***, **Judith Harrison**,* United States Naval Academy **INVITED**

Adhesion between DLC tips and diamond counterfaces was examined using a nanoindentor coupled to TEM and molecular dynamics (MD). Additional MD simulations of sliding contact between the same tip-substrate materials were also carried out. Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off forces and the nature of bond formation during sliding as a function of speed and hydrogen termination will be presented. The results of similar experiments and MD simulations using Si tips in contact with diamond counterfaces of adhesion and sliding using the ReaxFF potential will also be discussed.

9:40am **TR+AS+NS+SS-MoM5 The Chemistry of Friction, Wear, and Tribofilm Growth on 2D Materials***, **Jonathan Felts**,* Texas A&M University **INVITED**

The evolution of a sliding interface between two objects is difficult to theorize, predict, and measure due to the complexity of the interface, which is often described phenomenologically. Here we utilized a nanometer sized single asperity of an atomic force microscope tip sliding against atomically flat graphene and graphene oxide to study the origins of friction, wear, and tribofilm growth phenomena at the atomic scale. We hypothesize that all of the observed contact phenomena at the macroscale can be described using fundamental thermochemistry. At low applied tip loads, the friction of graphene oxide is non-monotonic with tip velocity, initially increasing for speeds from 100 – 10,000 nm/s, followed by a decrease and a subsequent increase above 50,000 nm/s. At sufficiently high applied loads, we observe wear of oxygen groups from graphene oxide at temperatures between 50-400 °C and loads between 10-700 nN, and find an exponential increase in wear rate with applied load. For the case of an electrically biased tip oxidizing pristine graphene, the oxidation rate somewhat paradoxically increases with applied load, despite previously observed enhancement in wear rate with load. All of the above observations can be understood in the context of mechanically driven thermochemical reactions. The friction behavior depends on two competing factors—aging of the sliding contact due to chemical bonding between tip and substrate, and hopping of unbonded tip atoms between graphene lattice sites. Atomic wear of graphene oxide is well described by the tilted potential energy surface theory of mechanically driven chemistry, which predicts a non-linear reduction in the energy barrier with applied load. We further show that the tilted potential energy surface model also well describes the enhancement of oxidation rate. The work presented here creates a foundation for describing the mechanics of sliding contacts as chemical processes, and further paves the way towards quantitatively understanding how mechanical force drives chemical reactions in general.

10:40am **TR+AS+NS+SS-MoM8 Nanomechanics of Soft, Hierarchical Polymer- and Biological-Networks***, **Prathima Nalam**,* University at Buffalo - SUNY **INVITED**

Soft networks based on synthetic polymer chains or biological filaments, with architecture that are anisotropic or hierarchical in nature, offer a path towards the development of tough and reliable flexible structures. These structures find applications in numerous areas including healthcare delivery, environmental purification systems, energy storage systems, flexible electronics, and tribology. Further, the ability of these networks to present a wide range of tunable functional properties, through alterations in the chemical structure of the monomers, synthesis or operational conditions, etc., which otherwise is rarely possible with other hard materials, promise the development of smart materials. In this study, we present the nanomechanical and nanotribological behavior of two stimuli-responsive networks consisting of (a) polyelectrolyte films with a thin layer of chitosan (CH) grafted on top of poly (acrylic acid) (PAA) brushes (CH/PAA) and (b) naturally grown mycelium-based networks. The CH/PAA network is a synthetic hierarchical structure, in which each layer exhibits a strong structural change with variation in solution pH. On the other hand, Mycelium is a soft biological network (derived from mushrooms) composed of multicellular or unicellular filaments, known as hyphae, with anisotropic micro-architecture.

A detailed investigation of the depth-dependent elastic moduli on these networks is conducted using atomic force microscope (AFM, Oxford Instruments) to study the impact of local structural heterogeneity of the network on its mechanical properties. A colloid-attached AFM cantilever was employed to study the surface interactions and to indent the material in the linear elastic deformation regime. The study of the impact of the network structure on the material rigidity, measured at both nano- and macro- scales, has enabled to probe the validity of affine network deformation theories for hierarchical networks. With this understanding, the design and development of antibacterial platforms (with CH/PAA platforms) and water-filtration membranes (with mycelium networks) using hierarchical soft structures is discussed.

11:20am **TR+AS+NS+SS-MoM10 Mechanisms for Controlling Friction and New Approaches for Achieving Superlubricity Regime in 2D Materials***, **Diana Berman**,* University of North Texas*; A. Erdemir, A.V. Sumant,* Argonne National Laboratory **INVITED**

Friction is an important aspect of many areas of everyday life. Varieties in mechanical systems from nano to macroscale and efforts to minimize energy losses intersect with challenges of controlling the friction. The popularity of recently discovered 2D materials and their usefulness for multiple applications enabled understanding the friction at a more fundamental level and opened new routes for manipulating friction to superlubricity or near zero friction values.

Here, we review the basic mechanisms that complies the frictional energy dissipation, such as wear, molecular deformation, thermal effect, electronic effect, bonding, environment and chemistry, phonons, and structural effect. We present the case studies highlighting how these mechanisms are controlled in 2D materials. Finally, we highlight recent advances in implementing 2D materials for friction reduction to superlubricity across scales from nano- up to macroscale contacts. We show that nanoscale superlubricity mechanisms originating from the formation of frictionless nanoscale systems, as in case of graphene-nanodiamond scrolls and carbon nanoonion structures, can be successfully transferred to macroscale effects. Development of 2D materials opened a new pathway for manipulating friction, which makes superlubric friction today's reality.

References:

[1] D. Berman, et al., Approaches for Achieving Superlubricity in Two-Dimensional Materials, ACS Nano (2018)

[2] D. Berman, et al., special issue in Diamond and Related Materials, 54, 91 (2015).

[3] D. Berman, et al., Materials Today 17 (2014) 31-42.

[4] D. Berman, et al., Science, 348 (2015) 1118-1122

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC+SS-MoA

X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies***, **Luca Gregoratti**, M. Amati, P. Zeller,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectro-microscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 µm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy***, **Jared Bruce**, J.C. Hemminger,* University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent, $Fe^{2+}_{(aq)}$, change with depth relative to the air/liquid interface. The chemical state is also sensitive to "spectator" ions in the solution. The presence of Cl^- leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy***, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; E. Strelcov,* NIST Center for Nanoscale Science and Technology*; **Tomas Duchon**,* Forschungszentrum Juelich GmbH, Germany*; H.X. Guo,* National Institute of Standards and Technology*; J. Hackl,* Forschungszentrum Juelich GmbH, Germany*; A. Yualev,* NIST Center for Nanoscale Science and Technology*; I. Vlassiouk,* Oak Ridge National Laboratory*; D.N. Mueller, C.M. Schneider,* Forschungszentrum Juelich GmbH, Germany*; A. Kolmakov,* NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable Cu+ ions.

3:40pm **MM+AS+NS+PC+SS-MoA8 Practical Liquid Cell Microscopy - Opportunities and Challenges***, **Daan Hein Alsem**, K. Karki,* Hummingbird Scientific*; J.T. Mefford, W.C. Chueh,* Stanford University*; N.J. Salmon,* Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiNx membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 01.M $CuSO_4$ and 20 mM $K_3Fe(CN)_6$/20 mM $K_4Fe(CN)_6$ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy***, **Hongxuan Guo**, A. Yulaev, E. Strelcov,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; A. Tselev,* CICECO and Department of Physics, University of Aveiro,Portugal*; A. Kolmakov,* National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods [1], and more recently with X-ray spectroscopy [2, 3], as well as scanning probe microscopy[4].

In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.[5,6]. We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

Reference

[1]. F. Zaera Chem. Rev. 112(2012),2920–2986

[2]. M. Favaro, B. Jeong, P. N. Ross, J. Yano, Z. Hussain, Z. Liu and E. J. Crumlin, Nature Communications 7(2016), 12695

[3]. M. A. Brown, Z. Abbas, A. Kleibert, R. G. Green, A. Goel, S. May, and T. M. Squires, Physical Review X 6(2016), 011007

[4]. J. M. Black, M. Zhu, P. Zhang, R. R. Unocic, D. Guo, M. B. Okatan, S. Dai, P. T. Cummings, S. V. Kalinin, G. Feng, and N. Balke, Scientific Reports 6 (2016), 32389

[5]. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlassiouk, A Kolmakov, ACS applied materials & interfaces 9 (2017), 26492-26502

[6]. H. Guo, E. Strelcov, A. Yulaev, J. Wang, N. Appathurai, S. Urquhart, J. Vinson, S. Sahu, M. Zwolak, and A. Kolmakov, Nano Letters,17(2017), 1034–1041

Surface Science Division
Room 203C - Session SS+HC-MoA

Theory and Modeling of Surfaces and Reactions

Moderators: Liney Arnadottir, Oregon State University, Petra Reinke, University of Virginia

1:20pm **SS+HC-MoA1 Elucidating the Chemical Nature of Single-Site Catalysts from First Principles**, *A.J.R. Hensley,* Washington State University; *A.J. Therrien,* Tufts University; *R. Zhang,* Washington State University; *A.C. Schilling,* Tufts University; *K. Groden,* Washington State University; *E.C.H. Sykes,* Tufts University; ***Jean-Sabin McEwen,*** Washington State University **INVITED**

Automotive catalysis is more complicated than most applications of catalysts, because of the complex and dynamic changes in the exhaust gas environment. The ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable [1]. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions [2]. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we have studied low-temperature CO oxidation on Pt single-site catalysts supported on the “29” Cu surface oxide. The “29” Cu surface oxide is a high coverage chiral structure. Through the use of scanning tunneling microscopy (STM), CO temperature programmed desorption (TPD), and density functional theory (DFT) techniques, we determined that an accurate model for the “29” Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings [3, 4]. Furthermore, the state of the Pt single atoms before, during, and after reaction is determined through a combination of theoretical and experimental techniques. It is found that the Pt dosed to the “29” Cu oxide surface forms well dispersed single atom sites which are metallic in nature [5]. During catalysis, CO_2 forms from the combination of an oxygen from the “29” Cu oxide surface with the CO adsorbed on the Pt single atoms.

1. Kwak, J.H., J. Hu, D. Mei, C.-W. Yi, D.H. Kim, C.H.F. Peden, L.F. Allard, and J. Szanyi, Science, 2009. **325**: p. 1670-1673.

2. Ding, K., A. Gulec, A.M. Johnson, N.M. Schweitzer, G.D. Stucky, L.D. Marks, and P.C. Stair, Science, 2015. **350**(6257): p. 189-192.

3. Therrien, A.J., R. Zhang, F.R. Lucci, M.D. Marcinkowski, A.J.R. Hensley, J.-S. McEwen, and E.C.H. Sykes, Journal of Physical Chemistry C, 2016. **120**: p. 10879-10886.

4. Hensley, A.J.R., A.J. Therrien, R. Zhang, M.D. Marcinkowski, F.R. Lucci, E.C.H. Sykes, and J.-S. McEwen, Journal of Physical Chemistry C, 2016. **120**: p. 25387-25394.

5. Therrien, A.J., A.J.R. Hensley, M.D. Marcinkowski, R. Zhang, F.R. Lucci, B. Coughlin, A.C. Schilling, J.-S. McEwen, and E.C.H. Sykes, Nature Catalysis, 2018. **1**: p. 192-198.

2:00pm **SS+HC-MoA3 Unravelling the Complex Features in STM Images of O/Ag(110) System**, ***Takat B. Rawal,*** University of Central Florida; *M. Smerieri,* IMEM-CNR, UOS Genova, Italy; *J. Pal,* University of Genova, Italy; *S. Hong,* Brewton-Parker College; *M. Alatalo,* University of Oulu, Finland; *L. Savio, L. Vattuone,* University of Genova, Italy; *T.S. Rahman,* University of Central Florida; *M. Rocca,* University of Genova, Italy

Elucidating the various structures involving oxygen adsorption on silver surfaces is a key issue in understanding the industrially relevant Ag oxidation process. Recently it was demonstrated that atomic oxygen can cause the extraction of substrate atoms off metal surfaces. In particular for Ag(110), the excavation process takes place already when O_2 is dosed at 175 K leading, at low coverage, to the formation of single Ag vacancies [1], which can serve as reactive sites. Vacancy creation proceeds thereby via the formation of O-Ag-O complexes, which involve a local reconstruction of the surface and ignite the disruption of the Ag substrate. Here, we present details of such processes and of the various structures formed by the O adatoms at very low coverage, for some of which the energetics had already been reported in ref. [2]. To this purpose we performed scanning tunnelling microscopy experiments and density functional theory calculations. A variety of features such as isolated grey dots, sombreros, shallow grey and white structures oriented along [001] and [1-10], grey stripes, and lozenges were identified and assigned to the O adatoms in different configurations. Most of the oxygen ends up either in “zig-zag chain” or in pinned, “lozenge” shaped structures. The former interact strongly with the STM tip and are easily disrupted, giving rise to highly mobile, sombrero shaped, isolated O adatoms. Around 200 K, not only Ag vacancies are mobile with anisotropic migration rates and can merge at larger coverage into complex features, but also the mobile Ag atoms are trapped by O adatoms leading finally to the O-Ag chains oriented along [001] forming the well-known added row reconstruction.

[1] J. Pal, T. B. Rawal, M. Smerieri, S. Hong, M. Alatalo, L. Savio, L. Vattuone, T. S. Rahman, and M. Rocca, Phys. Rev. Lett., **118**, 226101 (2017).

[2] T. B. Rawal, S. Hong, A. Pulkkinen, M. Alatalo, and T. S. Rahman, Phys. Rev. B. **92**, 035444 (2015).

*Work is partially supported by US NSF grant CHE-1310327.

2:20pm **SS+HC-MoA4 First Principles Investigations on CO_2 Adsorption and Dissociation on $Cu_{cluster}$ / Cu(111) Surfaces: Influence of Co-adsorbed CO Molecule**, ***Allan Abraham Padama,*** University of the Philippines Los Baños, Philippines; *H. Nakanishi, H. Kasai,* National Institute of Technology, Akashi College, Japan; *J.D. Ocon,* University of the Philippines Diliman, Philippines

Cheap Cu surfaces play important role in the synthesis of methanol and in reverse water gas shift reactions, in which, the interaction of the surfaces with carbon dioxide (CO_2) is an important process. Recent developments revealed the stable structures of Cu clusters on Cu(111) ($Cu_{cluster}$ / Cu(111)) that is activated by CO adsorption [Science 351 (6272), 475-478]. Interestingly, it is found that the surface facilitates water dissociation. In connection to these, we see the importance of studying the adsorption and dissociation of CO_2 on this system which could provide additional insights to the use of Cu-based surfaces as catalyst in various reactions.

In this work, we performed first principles calculations based on density functional theory (DFT) to investigate the adsorption and dissociation of CO_2 on $Cu_{cluster}$ / Cu(111), with and without the presence of co-adsorbed CO molecules. We modeled the system with three Cu atoms as cluster, which was experimentally identified as among the stable clusters on the Cu(111). The adsorption energy of CO_2 on $Cu_{cluster}$ / Cu(111) is ~0.25 eV, comparable to the obtained adsorption energy of CO_2 on flat Cu(111). We found that the cluster and the presence of CO do not influence the dissociation of CO_2. An activation energy of ~1.6 eV accompanies the dissociation when it takes near the cluster which is similar to the barrier on pristine Cu(111). The dissociation barriers on the cluster region are ~1.0 – 1.2 eV, lower than on Cu(111), and it appears that co-adsorbed CO molecules do not significantly affect the dissociation process. CO_2 that dissociates directly on the cluster is only accompanied by ~0.6 eV activation barrier, but further diffusion of the adsorbed species away from the cluster increases the barrier. The geometric and electronic properties analyses that support the obtained results will be presented in the symposium.

2:40pm **SS+HC-MoA5 Step-Spacing Distributions Revisited: New Motivations from Curved Crystals and Other Systems***, **Theodore L. Einstein**,* University of Maryland, College Park

Recent experiments on curved crystals of noble and late transition metals (Ortega and Juurlink groups) have renewed interest in terrace width distributions (TWD) for vicinal surfaces. We first summarize refinements of TWD analysis that are absent from the standard reviews. Rather than by Gaussians, TWDs are better described by a single-parameter distribution with a power-law rise and a Gaussian decay, thereby including effects evident for weak step repulsion: skewness and peak shifts down from the mean spacing. Curved crystals allow analysis of several spacings with the same substrate, so that one can check the scaling with the mean width. This is important since such scaling confirms well-established theory. Failure to scale also can provide significant insights. Complicating factors can include step touching (local double-height steps), oscillatory step interactions mediated by metallic (but not topological) surface states, short-range corrections to the inverse-square step repulsion, and the offset between adjacent layers of almost all surfaces. We discuss how to deal with these issues. Many of the curved-crystal experiments involve in-plane misoriented (zig-zag) steps. There are formulas to describe the stiffness but not yet the strength of the elastic interstep repulsion. Some theory results are available for these orientations; more are needed. Other intriguing results have been reported for spacings of spiral steps around a dislocation.

3:40pm **SS+HC-MoA8 Elucidating Mechanisms of Alkanol Catalysis on $SrTiO_3$ Perovskite Surfaces using Density Functional Theory***, **Robert Chapleski**, S. Roy,* University of Tennessee Knoxville

Targeted at understanding observed differences in reaction dynamics for various alkyl alcohols on catalytic $SrTiO_3$ surfaces, we describe the results of our computational study of isopropanol adsorption and catalysis on $SrTiO_3$ (100). Using the PBE density functional with a Hubbard-U correction to initially probe the potential energy surface of adsorption, we have found a minimum-energy orientation for isopropanol adsorbed on the surface in good agreement with recent sum-frequency generation experiments. Continuing with this minimum, we followed multiple competing pathways and determined necessary transition states and intermediates in order to describe the kinetics and thermodynamics of these reactions. Armed with these results, we elucidate recent experimental findings favoring the formation of the dehydrogenation product acetone over the dehydration product propylene. Finally, we probed the adsorption potential energy surfaces of products in order to describe the contributions of product orientation and lateral surface diffusion to overall reaction dynamics. Our future work will consider different $SrTiO_3$ surfaces such as (111) and (110), as well as different alkanol adsorbates such as ethanol. Overall, these studies provide insight into the fundamental aspects of catalysis of this class of reagents on perovskite surfaces.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-TuM

Nanochemistry in Heterogeneous Catalysis

Moderator: Matthew Marcinkowski, Pacific Northwest National Laboratory

8:00am **HC+SS-TuM1 Probing Oxide Supported Single Rh Atoms as Model Catalysts for CO Oxidation**, ***Alex C. Schilling***, *E.C.H. Sykes,* Tufts University

In recent years, single atom active sites have become a central topic in the creation of new catalysts with a focus on supported Rh atoms as a means of activating C-H bonds and catalyzing the water-gas shift reaction. These heterogeneous catalysts can operate at the single atom limit, decreasing the amount of precious metal on the support and thereby the price of the catalyst. However, debate still exists in the literature over the nature of the active sites and their mechanism of operation. We have taken a reductionist model study approach towards understanding these issues in well-defined single atom systems. Using surface-sensitive techniques, such as Temperature Programmed Desorption (TPD) and Reflection Absorption Infrared Spectroscopy (RAIRS), we assess the ability of single Rh atoms to oxidize CO. Experiments show that this system has the potential to convert the majority of Rh adsorbed CO to CO_2 at relatively low temperature. At low coverages of Rh (0.5-6%) preliminary experiments show two distinct desorption states for CO_2 at 325 K and 462 K. These TPD peaks account for 85% of all CO desorption from the Rh sites. The other 15% desorbs from Rh as CO at the same temperatures. Further work on this system will give insight into the nature of the active Rh sites, their interaction with both CO and support oxide, as well as the reaction mechanism.

8:20am **HC+SS-TuM2 Methanol Partial Oxidation Mechanisms on a Single-site Catalyst Pt_1/ZnO(10-10): A First-principles Study**, ***Tao Jiang,*** University of Central Florida; *T.B. Rawal,* Oak Ridge National Laboratory; *D. Le, T.S. Rahman,* University of Central Florida

The rational design of single metal atoms anchored on non-metallic surface has the great potential to offer catalysts with high activity and selectivity [1]. Towards this goal, we have carried out density functional theory based calculations of the catalytic behavior of singly dispersed Pt atoms on ZnO, Pt_1/ZnO(10-10), as a model system for methanol partial oxidation. We find that methanol adsorption is favored at the surface Zn site whereas oxygen prefers to adsorb at the Pt-Zn site. The adsorption of reaction intermediates CO, CO_2, and H_2 are favored at the Pt site, whereas H_2O prefers to sit at the Zn site. Secondly, along the reaction pathways for methanol dehydrogenation, we will illustrate that the O-H bond scission from methanol is slightly exothermic (ΔE=-13 meV). The resultant methoxy then preferentially adsorbs at the Pt-Zn site, where C-H bond of methoxy can be easily activated. The dissociation of methoxy (CH_3O' ' ->CH_2O+H) is exothermic (ΔE=-0.42 eV) and that of formaldehyde (CH_2O->' CHO+H) is endothermic (ΔE=+0.16 eV). The results suggest that Pt_1/ZnO(10-10) is a potential single-atom catalyst for methanol oxidation. We will compare our findings with those for the related system Pd_1/ZnO(10-10) [1] and available experimental observations to evaluate their relative advantages for methanol partial oxidation.

[1] T. B. Rawal, S. R. Acharya, S. Hong, D. Le, Y. Tang, F. F. Tao, and T. S. Rahman, submitted (2018).

The work is partially supported by DOE grants DE-FG02-07ER15842

8:40am **HC+SS-TuM3 Imaging the Ordering of Weakly Adsorbed CO_2 Molecules on Rutile Titania using Ambient Pressure Microscopy and Spectroscopy**, ***Rebecca Hamlyn***[1], Brookhaven National Lab; *J.A. Rodriguez, S. Senanayake, M. Mahapatra, F. Xu, D. Grinter, S. Luo, P. Liu, R. Palomino, I. Waluyo, S. Kattel, D.J. Stacchiola,* Brookhaven National Laboratory

Recently, great effort has been devoted to the capture, activation and conversion of carbon dioxide (CO_2), a ubiquitous greenhouse gas and by-product of many chemical processes. The high stability and non-polar nature of CO_2 leads to weak bonding with well-defined surfaces of metals and oxides. The interactions of CO_2 involve intermolecular forces with noncovalent bonding (van der Waals), and often a surface needs to be functionalized to create polar sites that can "capture" or bind CO_2. Images from ambient pressure scanning tunneling microscopy show that a substantial amount of CO_2 can reside on a TiO_2(110) surface at room temperature as a consequence of weak bonding interactions with the substrate. Furthermore, the adsorbates exhibit a disorder-order transition on this surface, despite the lack of a strong interaction that may serve to impose its substrate periodicity on the adsorbed film. This phenomena is of interest to many areas of the surface science and chemistry community wherein condensation of van der Waals gases such as CH_4, N_2, or CO_2.

We have employed microscopic imaging under *in situ* conditions, soft X-ray spectroscopy and theory to decipher the unique ordering behavior seen for CO_2 on TiO_2(110).

9:00am **HC+SS-TuM4 Using Sn Atomic Layer Deposition to Tune the Coking Resistance of Size-selected Pt Model Catalysts**, ***Timothy Gorey***[2], *E. Baxter, A. Cass, S. Anderson,* University of Utah; *B. Zandkarimi, A. Alexandrova,* University of California at Los Angeles

Size-selected cluster catalysts are powerful tools that enable us to probe and characterize specific catalytic reaction mechanisms controlled by the particle's size. By combining deposition of atomically-selected Pt clusters, with ALD to selectively add Sn atoms to the clusters, we obtain Pt-Sn alloy clusters with exactly known numbers of Pt atoms, and a narrow distribution of Sn atoms. In addition to being a powerful experimental tool, having size-selected model catalysts with well-defined compositions allow detailed theoretical simulations, providing insight into cluster structure, and the mechanistic origins of the size and alloying effects observed experimentally. It is found that tin alloying has a large and beneficial effect on both the branching between intact ethylene desorption vs. dehydrogenation/carbon deposition, and on the thermal stability of the clusters at temperatures to 700 K. Theoretical predictions for the structures and electronic properties of the thermally accessible ensemble of isomers are used to rationalize the observed effects in detail.

*Work supported by the United States Air Force Office of Scientific Research (AFOSR FA9550-16-1-0141)

9:20am **HC+SS-TuM5 Synergistic Effects of Pd and PdO Domains on Thin Film TbOx(111)/Pt(111)**, ***Christopher Lee***[3], *J.F. Weaver,* University of Florida

Among the rare earth oxides (REOs), the terbium oxides exhibit favorable properties in selective oxidation catalysis due to the flexibility in the storage and release of oxygen within the lattice. Of particular note is the ease of structural rearrangement into well-ordered intermediates between the Tb_2O_3 and TbO_2 stoichiometries, providing a novel, dynamic surface interface for the promotion of oxidation reactions. We investigated the stabilization and reactivity of metallic Pd domains grown on top of ultrathin c-Tb_2O_3(111)/Pt(111) films in ultrahigh vacuum (UHV) and subsequently oxidized by plasma-generated gaseous atomic oxygen. XPS shows that while both the film and metallic domains are almost fully oxidized to both TbO_{2-} and PdO by atomic oxygen, subsequent annealing to ~600 K can significantly reduce the TbO_x supporting film while leaving the PdO largely unreduced. Our results provide evidence that the presence of Pd structures on the TbO_x surface greatly promotes the thermal reduction of TbO_2. Further annealing of the system at ~900 K results in PdO decomposition and agglomeration of metallic Pd domains as evidenced by the diminution of the XPS Pd 3d peaks.

The oxidation/reduction behavior of the Pd/TbO_x(111) system has enabled the study of oxidative reactions on three characteristic interfaces: PdO on TbO_2(111), PdO on Tb_nO_{2n-m}(111), and Pd on c-Tb_2O_3(111). TPD and TPRS experiments show that adsorbed CO and C_3H_8 only react with the stabilized PdO domains, with C_3H_8 desorption at ~200 K being characteristic of adsorbed propane σ-complexes observed previously on PdO(101) surfaces. Continual reduction of PdO with adsorbed CO and C_3H_8 also show that when thermal reduction is limited to ~600 K, the underlying TbO_x support will continually replenish the reduced PdO domains with oxygen. This is also noted by the substantially higher conversion of adsorbed CO to CO_2 compared with that seen on pure PdO(101) as conversion would be less limited if reactive oxygen is supplied from both PdO and the TbO_x support. This behavior suggests a strong synergy between the surface Pd/PdO domains and the underlying TbO_x film, such as a Mars-van Krevelen interaction in which TbO_x readily transfers O-atoms to Pd and thereby sustains oxidation chemistry.

---

[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[2] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[3] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

9:40am **HC+SS-TuM6 Copper Vapor Adsorption Calorimetry on $HCa_2Nb_3O_{10}$(001) Nanosheets: Energetics and Adsorbate Structure*, Wei Zhang*[1]**, *J.E. Eichler,* University of Washington*; R. Uppuluri, T.E. Mallouk,* The Pennsylvania State University*; C.T. Campbell,* University of Washington

The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the chemical bonding strength at such interfaces is of great interest. These strengths have been measured on single-crystal oxide films of a single metal element by metal vapor adsorption calorimetry in ultrahigh vacuum (UHV), but never before on mixed oxides of two or more metal elements, yet mixed oxides are often used as supports in catalysis with considerable improvement on various aspects of catalyst performance. The preparation of atomically-smooth single-crystal mixed-oxide films in well-defined composition that would be applicable in our adsorption calorimetry is very challenging. Mallouk et. al. have reported a class of lamellar $HCa_2Nb_3O_{10}$(001) nanosheets which can be deposited in a layer-by-layer fashion on flat substrates using Langmuir-Blodgett (LB) techniques to make thin and well-ordered mixed-oxide films. These nanosheets can extend laterally for long distances (>1 µm) indicating that they have very high surface area with homogeneous surface sites and a huge ratio of terrace sites to sheet-edge sites. Furthermore, when used as supports for transition metal oxide (or hydroxide) nanoparticles, they display unusual stability against sintering. Here, we apply the surface chemistry techniques derived for single-crystal oxide films to the much more complex perovskite mixed-oxide films by investigating the adsorption of Cu atoms on the $HCa_2Nb_3O_{10}$(001) nanosheets (~6.3 nm thick) at both 300 K and low temperature (<150 K). Cu atoms show an initial heat of 186 kJ/mol at 300 K, which is close to the DFT value for Cu monomers. The heat of adsorption then increases quickly to the heat of sublimation of bulk Cu(s) (337 kJ/mol). Low-energy He^+ ion scattering spectroscopy (LEIS) allows us to investigate the morphology and the number density of Cu particles. The possible chemical reactions between the Cu atoms and the $HCa_2Nb_3O_{10}$(001) nanosheets during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

11:00am **HC+SS-TuM10 Adsorption and Adhesion of Ni on MgO(100) at 300 and 100 K by Calorimetry*, Zhongtian Mao*,** *W. Zhao, Z. Almualem, C.T. Campbell,* University of Washington

Metal nanoparticles anchored on the surface of oxide support form the basis of modern heterogeneous catalysts used for clean energy, pollution prevention and industrial-scale chemical production. Since the catalytic activity, selectivity and long-term stability of supported nanoparticles correlate with metal chemical potential which in turn decreases strongly with the metal/oxide interface adhesion energy, E_{adh}, it is crucial to understand how the properties of both metal and oxide control E_{adh}. Adhesion energies of metal nanoparticles to clean oxide surfaces were previously measured in ultra-high vacuum using either single-crystal adsorption calorimetry (SCAC) or particle-shape measurements by electron microscopy or grazing-incidence X-ray scattering. The results reveal a trend that E_{adh} on a given oxide surface increases linearly from metal to metal with increasing metal oxophilicity, defined as the magnitude of the heat of formation of the most stable oxide from gas-phase metal atoms.[1] The oxophilicity of Ni is so high that it is predicted by this trend to have 50% higher adhesion than any of the other metals that have been studied on MgO(100) (i.e., Pb, Ag, Au, Pd Cu and Pt). We report here caloriometric heats of adsorption of Ni gas onto MgO(100) which validate this prediction and thus prove the predictive ability of this trend. Oxide-supported Ni nanoparticles are widely used as industrial catalysts, so these results are of interest in catalysis research. The adsorption of Ni vapor onto MgO(100) films grown on Mo(100) is studied at 300 and 100 K using single crystal adsorption calorimetry. The Ni particle morphology is investigated using He^+ low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). Combining the heat of adsorption and this information on Ni particle morphology also allows the adhesion energy of Ni(solid) to MgO(100) to be found. The initial heat of adsorption at 300 K is 276.5 kJ/mol, 35.7 % lower than the saturation heat at high coverage (equal to the bulk heat of Ni sublimation). This initial heat corresponds to making Ni cluster that are ~0.53 nm in diameter. We also report the chemical potential of Ni versus particle size on MgO(100).

[1] Hemmingson, S. L.; Campbell, C. T. ACS Nano 2017, 11, 1196−1203.

11:20am **HC+SS-TuM11 *In situ* Microscopy of Oxide Growth and Transformation under Reaction Conditions*, Jan Ingo Flege,*** University of Bremen, Germany **INVITED**

Current research in heterogeneous catalysis aims to provide a deeper understanding of all the components in a real catalytic system, which depending on the conditions typically comprises both metals and oxides in nanoparticulate form. Significant progress has been achieved by studying carefully devised model systems that facilitate detailed investigation of the structure and chemistry of the individual constituents in controlled environments. While traditional approaches have focused on the role of oxide-supported metal nanoparticles, in the so-called inverse configuration a nanosized metal oxide is supported on a transition metal, thereby allowing us to assess the properties of the nanoscale metal oxide and its defect chemistry as well as to gain complementary access to the oxide-metal interface.

In this presentation, we will focus on the epitaxial growth of ultrathin metal oxide films and nanostructures on transition metals, with a special emphasis on rare-earth oxides. These materials have attracted considerable attention owing to their rich chemistry and enhanced reducibility in proximity to transition metals. We will demonstrate that real-time monitoring of their synthesis under vacuum conditions as well as their structural and chemical modifications on the nanometer scale in reactive gaseous environments is possible using low-energy electron microscopy and related methods [1]. Primary examples will address reversible structural transformations in ruthenium, platinum, and copper supported cerium oxide inverse model catalysts [2-5] upon thermal and chemical reduction, e.g., from CeO_2 via the cubic Ce_2O_3 phase to hexagonal Ce_2O_3, concomitant with partial dissolution of the cerium oxide particles and considerable dispersion of metallic cerium on the substrate, resulting in irreversible morphological changes. Similar sesquioxide and dioxide phases are present directly after deposition of praseodymium oxide on the Ru(0001) surface [6, 7], illustrating an intrinsic nanoscale complexity and the importance of the oxide-metal interface.

[1] J. I. Flege and D. C. Grinter, Prog. Surf. Sci. (2018), in press. DOI: 10.1016/j.progsurf.2018.02.001

[2] D. C. Grinter, S. D. Senanayake, and J. I. Flege, Appl. Catal., B 197, 286 (2016).

[3] J. Höcker et al., Adv. Mater. Interfaces 2, 1500314 (2015).

[4] J. Höcker, J.-O. Krisponeit, Th. Schmidt, J. Falta, and J. I. Flege, Nanoscale 9, 9352 (2017).

[5] M. Sauerbrey, G. Gasperi, P. Luches, J. Falta, S. Valeri, J. I. Flege, Top. Catal. 60, 513 (2017).

[6] J. Höcker et al., Phys. Chem. Chem. Phys. 19, 3480 (2017).

[7] J. I. Flege et al., Ultramicroscopy 183, 61 (2017).

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices***, Y.S. Meng,* University of California San Diego*; **Yangyuchen Yang,*** University of California at San Diego **INVITED**

Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes

---

[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM3 An *In situ* Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces*, James De Yoreo,*** Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered.Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation.Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate.The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface***, Geiger, **Ariana Gray Be**,* Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS*, Meng Jia,*** Unversity of Delaware*; A. Broderick, J.T. Newberg,* University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts (ΔBE/ΔE) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a ΔBE/ΔE value of less than one. Upon introducing water vapor, forming an IL/water mixture, the ΔBE/ΔE approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM11 Role of Air Gas at the Interface between Water and Graphite Surfaces*, Ing-Shouh Hwang,*** Institute of Physics, Academia Sinica, Taiwan, Republic of China*; C.W. Yang, C.K. Fang,* Institute of Physics, Academia Sinica,Taiwan, Republic of China*; Y.H. Lu,* Institute of Physics, Academia Sinica, Taiwan, Republic of China*; H.C. Ko,* Institute of Physics, Academia Sinica,Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

[1] H.-C. Ko, W.-H. Hsu, C.-W. Yang, C.-K. Fang, Y.-H. Lu, I.-S. Hwang, *Langmuir***32**, 11164 (2016)

[2] Y.-H. Lu, C.-W. Yang, and I.-S. Hwang, *Langmuir***28**, 12691 (2012).

[3] Y.-H. Lu, C.-W. Yang , C.-K. Fang, H.-C. Ko, I.-S. Hwang, *Sci. Rep.***4**, 7189 (2014).

[4] C.-K. Fang, H.-C. Ko, C.-W. Yang , Y.-H. Lu, I.-S. Hwang, *Sci. Rep.* 6, 24651 (2016).

11:40am **PC+AS+BI+NS+PB+SS-TuM12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry*, Musahid Ahmed,*** *O. Kostko,* Lawrence Berkeley National Laboratory **INVITED**

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.^{1} I will follow up with very recent results on association of water with “hydrophobic” naphthalene & “hydrophilic” glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample's electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams[2] that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its' implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).[3] A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.[4]

[1] T. Stein, B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, M. Head-Gordon, PNAS (2017), DOI 10.1073/pnas.1616464114

[2] O. Kostko, B. Xu, M.I. Jacobs, M. Ahmed, J. Chem. Phys. DOI: 10.1063/1.4982822

[3] B. Xu, M.I. Jacobs, O. Kostko, M. Ahmed, Chem. Phys. Chem. DOI 10.1002/cphc.201700197

[4] J. Yao, D. Lao, X. Sui, Y. Zhou, S. K. Nune, X. Ma, T. P. Troy, M. Ahmed, Z. Zhu, D. J. Heldebrant, X-Y. Yu, Phys. Chem. Chem. Phys. DOI: 10.1039/C7CP03754F

Surface Science Division

Room 203C - Session SS+HC+NS+PS-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:40am **SS+HC+NS+PS-TuM3 Stability and Reactivity of Isolated Rh_1 Atoms on Fe_3O_4(001)**, ***Gareth Parkinson***, TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe_3O_4(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe_3O_4(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh1 species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh1 diffusion is induced upon adsorption of O_2 and NO.

9:00am **SS+HC+NS+PS-TuM4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne**, *T. Wang, H.F. Lv, L. Feng, J.M. Huang, X.J. Wu,* University of Science and Technology of China; ***Junfa Zhu,*** National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by single-molecule dehydrogenation, similar as the mechanism of on-surface Ullman coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullman reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am **SS+HC+NS+PS-TuM5 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde**, ***Xingyi Deng***, *D.C. Sorescu, J. Lee,* National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-^{18}O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-^{18}O at T = 100 K, whereas a partial oxidation product, formaldehyde-^{18}O (~95% selectivity), and a small amount of carbon dioxide ($C^{16}O^{18}O$) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH_3O(ad)) intermediate, following the pathways $CH_3OH(ad) \rightarrow CH_3O(ad) + H(ad) \rightarrow CH_2O(g) + 2H(ad)$ with an overall barrier of 19.0 kcal/mol. Formation of CO_2 was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde ($H_2COO_{lattice}$(ad)), the proposed precursor leading to CO_2. These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface**, ***Junseok Lee***, *D.C. Sorescu, X. Deng,* National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM11 Oxygen Reduction Reaction on Fullerene**, ***Yosuke Kikuchi***, *J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp^2 to sp^3-like sp^2, and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C_{60}) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al*. [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), oxygen molecule (O_2) is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the $4e^-$ pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are overstabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

[1] K. R. Lee, K. U. Lee, J. W. Lee, B. T. Ahn, S. I. Woo, Electrochem. Commun. 12, 1052 (2010)

[2] S. Ni, Z. Li, J. Yang, Nanoscale, 4, 1184 (2012)

[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Phys. Chem. B 108, 17886 (2004)

11:40am **SS+HC+NS+PS-TuM12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys***, **Dipna Patel**, E.C.H. Sykes,* Tufts University

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules***, **Kotarou Takeyasu**, Y. Shimoyama, M. Furukawa, S. Singh, J. Nakamura,* University of Tsukuba, Japan

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyridophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M H_2SO_4) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyridophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of 10 mA cm^{-2}) were 0.29 V, 0.28 V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyridophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H…N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

References

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science, 2016, 351, 361-365.

[2] R. Shibuya, T. Kondo, J. Nakamura, ChemCatChem, 2018

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-TuA

A Tale of Two Scales: Catalytic Processes and Surface Science

Moderator: Ashleigh Baber, James Madison University

2:20pm **HC+SS-TuA1 CO_2 Reduction on the Surface of Cu/TiO_2 NPs Supported on Graphite Studied using Ambient Pressure-XPS and Differential Electrochemical Mass Spectrometer***, **Djawhar Ferrah**, A. Haines, R.P. Galhenage,* University of California at Irvine*; A. Javier,* California Institute of Technology*; J.P. Bruce,* University of California at Irvine*; M. Soriaga,* California Institute of Technology*; J.C. Hemminger,* University of California at Irvine

Metal supported on metal oxide (M1/MO) catalyst systems are widely used in industry for the hydrogen production and CO_2/CO conversion to useful fuels. If incontrovertible evidence were founded for the role of the interface in the improvement of catalytic CO_2 hydrogenation efficiency, it would still be an incomplete understanding on the nature of the active sites and associated reaction pathways, namely reactive species adsorption, dissociation and/or activation and intermediate formation stability. The modulation of the reaction selectivity, through the synthesis of catalysts that exhibit specific active sites, is required to design «smart » catalytic systems. Therefore, the investigation of catalytic reactions under real conditions, to illustrate the relation between properties at the atomic level of the surface and reactivity, is needed. In this context, a model catalyst based on Cu/TiO_2 nanoparticles (NPs) supported on graphite (HOPG), have been synthesized and fully characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Using physical vapor deposition (PVD), a high density of 15 nm TiO_2 NPs are deposited on HOPG and are used to support Cu NPs. TEM studies reveal that most of the TiO_2 NPs have a rutile structure and display mainly (110) vicinal surface, which is favorable for CO_2 adsorption. A formation of thin layer of graphitic carbon at surface of TiO_2 NPs is also reported. Photodeposition of Cu on TiO_2 NPs by irradiating the band gap of TiO_2 in a $CuCl_2$ solution has been studied. In the present work, two different catalytic aspects for CO_2 reduction on CuO_x/TiO_2 NPs on HOPG systems will be reported: (1) thermocatalytic CO_2 hydrogenation and (2) electrochemical CO_2 hydrogenation. Efforts have been devoted to exploring different surface chemistry effects, as well as the oxidation states of Cu NPs (Cu_2O, Cu, and Cu_2O@Cu) with diameters ranging from 2 to 5 nm and TiO_2 surface encapsulation with thin layer of graphited carbon, on the CO_2 reduction mechanism in the temperature range of 300-550 K using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the National Synchrotron Light Source II (NSLS-II). Similarly, the CO_2 reduction on CuO_x/TiO_2 NPs on HOPG electrodes in aqueous $KHCO_3$ has been investigated using a Differential Electrochemical Mass Spectrometer (DEMS) to evaluate the reaction products. Ongoing Infrared reflection-absorption spectroscopy (IRRAS), and AP-XPS experiments on electrochemical CO_2 reduction will be introduced.

2:40pm **HC+SS-TuA2 Influence of Bi and Sb on the Structure of Pd-based Catalysts***, **Joo Kang**, W.-S. Lee, P.R. Vlasak,* The Dow Chemical Company*; A.V. Kirilin,* The Dow Chemical Company, Netherlands*; H. Clements, C. Menzies, S. Yusuf,* The Dow Chemical Company

Oxidative transformation of aldehydes to corresponding esters is a reaction of significant importance. Catalytic oxidative esterification of aldehydes and alcohols in the presence of heterogeneous catalysts is an attractive method for production of esters. Reaction can be carried out in the presence of palladium or platinum often with co-components to improve performance.

The influence of 4d and 5d metal promoters on Pd based catalysts was investigated using a suite of structure probing techniques including x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and X-ray Absorption Spectroscopy (XAS). Results on supported Pd, Pd-Bi and Pd-Sb catalysts allow new insight into active Pd structure and role of the promoters on Pd structure. We present formation of bimetallic phase in both Bi and Sb promoted Pd catalysts and discuss implication on catalytic performance.

3:00pm **HC+SS-TuA3 The Molecular Surface Chemistry Approach to Heterogeneous Catalysts***, **Peter Stair**,* Northwestern University **INVITED**

The traditional route to solid catalyst materials involves solution phase deposition or liquid-surface reactions. Examples include impregnation, deposition-precipitation, and solution phase grafting of molecular precursors. Atomic Layer Deposition (ALD) is a gas-solid deposition methodology having enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions. This lecture will provide examples from the laboratories at Northwestern University and Argonne National Laboratory of ALD used to synthesize oxide supports, catalytic oxide overlayers, single-site catalysts, metal nanoparticles, and new porous structures.

4:20pm **HC+SS-TuA7 Formation and Stability of Subsurface Oxygen on Ag(111)***, **Marie Turano**,* Loyola University Chicago*; S. Isbill, S. Roy,* University of Tennessee Knoxville*; R.G. Farber,* Loyola University Chicago*; E.V. Iski,* University of Tulsa*; D.R. Killelea,* Loyola University Chicago

A long-standing challenge in the study of heterogeneously catalyzed oxidation reactions on silver surfaces is the determination of what surface species are of greatest chemical importance. This is due to the coexistence of several different types of oxygen on oxidized silver surfaces. A further wrinkle is subsurface oxygen (Osub). Osub are O atoms dissolved into the near surface of a metal, and are expected to alter the surface chemistry and structure, however, these effects have yet to be well characterized. To better understand the interactions of oxidized silver surfaces, synergy between experimental and theoretical studies is necessary. We have studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms using a combination of surface science techniques to determine the resultant surface structure. We observed that once 0.1 ML of Osub has formed, the surface dramatically, and uniformly, reconstructs to a striped structure at the expense of all other surface structures. Furthermore, Osub formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures (475-525K), and the predominance of the p(4x5√3) surface reconstruction at elevated temperatures. Recent DFT-calculated desorption energies of O atoms from Ag(111) agree well with experimentally-derived desorption energies, and provide qualitative insight into the formation and stability of Osub at different oxygen coverages.

4:40pm **HC+SS-TuA8 Mechanistic Insights into Catalytic Transfer Hydrogenation and Decarbonylation of Aromatic Aldehydes on P_x-Ru(0001)***, **Abinaya Sampath**, D.W. Flaherty,* University of Illinois at Urbana-Champaign

Aromatic aldehydes constitute a significant weight fraction of bio-oil.Transition metal catalysts can hydrogenate these aldehydes using either gaseous H_2 or organic donors to produce valuable chemicals that may replace conventional petroleum derivatives. Here, we study selective decarbonylation of aromatic aldehydes (furfural and benzaldehyde) over Ru(0001) and P_x-Ru(0001) to determine how phosphorus introduces new reaction pathways, such as catalytic transfer hydrogenation (CTH) steps between organic reactants. The catalytic properties of Ru(0001) and P_x-Ru(0001) were probed with temperature programmed reaction (TPR) of furfural, benzaldehyde, and isotopically labeled forms of furfural under ultra-high vacuum conditions with Ru(0001) single crystal. P_x-Ru(0001) is formed by exposing Ru(0001) to 2.5 L of PH_3 at 300 K followed by flash annealing to 1400 K. The treatment produces a surface with an atomic ratio of P: Ru of ~0.4, determined by Auger electron spectroscopy.

On $P_{0.4}$-Ru(0001), ~68% of furfural adsorbed at 100 K decarbonylates to furan and CO, whereas on Ru(0001), furfural decomposes completely to CO, H_2, and C-atoms. Similarly, benzaldehyde decarbonylates to benzene with a selectivity that is 12-fold greater over $P_{0.4}$-Ru(0001) than on Ru(0001). Together, these results suggest that, P-modification of Ru(0001) results in selective decarbonylation of aromatic aldehydes. Charge transfer from Ru to P results in reduced electron back donation from Ru to the adsorbates, and causes adsorbates to interact more weakly with $P_{0.4}$-Ru(0001) than with Ru(0001). These electronic modifications reduce the extent of dissociative reactions leading to selective decarbonylation of aromatic aldehydes, although ensemble effects may also contribute.

TPR of furfural on $P_{0.4}$-Ru(0001), pre-covered with D* atoms, yields five times more per-hydrogenated furan (C_4H_4O) than mono-deuterated furan (C_4H_3DO), which demonstrates that the CTH does not involve chemisorbed

H*-atoms. On $P_{0.4}$-Ru(0001), TPR of isotopically labeled furfural (C_4H_3O-CDO) forms two furan isotopologues (C_4H_4O, and C_4H_3DO). In addition, C_4H_3DO formed desorbs at a temperature 20 K higher than C_4H_4O, which indicates that intermolecular H-transfer determines the rate of furan formation. The comparisons of labeled furan products show that these critical H-atoms originate from the furfural ring and the carbonyl group of furfural. Hence, $P_{0.4}$-Ru(0001) is more selective for decarbonylation of aromatic aldehydes over Ru(0001), and the addition of phosphorus atoms facilitates CTH steps that do not occur on metallic Ru(0001).

5:00pm **HC+SS-TuA9 Hot Electron Flux under Methanol Oxidation on Pt/TiO_2 Catalytic Nanodiode; Intrinsic Relation between Selectivity and Chemicurrent*, Si Woo Lee*,** *S. Lee,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H. Lee,* Institute for Basic Science (IBS), Republic of Korea*; W. Park, Y. Jung, J.Y. Park,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Nonadiabatic electronic excitation in exothermic chemical reactions leads to the flow of energetic electrons with an energy of 1-3 eV which is called “hot electrons”. Direct detection of hot electron flow and observation of its role in catalytic reactions are important for understanding metal-oxide heterogeneous catalysis [1, 2]. Using Pt/n-type TiO_2 Schottky nanodiode, we show the production of hot electron flow generated by methanol oxidation ($P_{methanol}$ 4 Torr and P_{oxygen} at 760 Torr) on Pt thin film, and detect as steady-state hot electron current (chemicurrent) which is generated by exothermic chemical reactions on Pt catalyst surface. Under methanol oxidation, methanol can be converted to CO_2 by full oxidation or methyl formate by partial oxidation of methanol. We show that the activation energy of chemicurrent is quite close to that of turnover frequency, indicating that the chemicurrent was originated from the catalytic reaction on Pt thin film. In addition, the dependence of the partial pressure on the chemicurrent was investigated by varying partial pressure of methanol (1-4 Torr). The result shows that the selectivity toward methyl formate formation is well correlated with the chemicurrent. For fundamental understanding of correlation between selectivity and chemicurrent, we carried out the DFT calculation on the thermodynamic energy for each step, and found that the energy gain for partial oxidation reaction was higher than that of the full oxidation reaction, which is responsible for the higher flux of hot electron under methyl formate formation. We discuss the role of metal-oxide interfaces in determining the catalytic selectivity and chemicurrent yield.

Reference

1. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal–Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chem. Rev.* **2015,** *115* (8), 2781-2817.

2. Park, J. Y.; Kim, S. M.; Lee, H.; Nedrygailov, I. I., Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity. *Acc. Chem. Res.* **2015,** *48* (8), 2475-2483.

5:40pm **HC+SS-TuA11 Non-Innocent Solvents, Hydrogen Transfer, Oxygen Dissociation on Nanoparticles during the Direct Synthesis of H_2O_2*, David W. Flaherty,*** University of Illinois, Urbana-Champaign **INVITED**

Direct synthesis of H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) could enable on-site, and even *in situ*, H_2O_2 production, which motivates searches for highly selective catalysts and process conditions. H_2O_2 formation rates and selectivities depend sensitively on the addition of other transition metals, adsorption of halides, and solvent identity. The reasons for these changes are not completely understood and are difficult to explain mechanistically.

Rate measurements, X-ray absorption spectroscopy, and computation were conducted for Pd and Pd-based bimetallic clusters to determine the mechanism of this reaction and to understand the reasons why alloying Pd often increases H_2O_2 selectivities. In aqueous alcohols, the change in H_2O_2 and H_2O formation rates with H_2 and O_2 pressures are not consistent with a Langmuirian mechanism, but instead suggest O_2* species react in steps mediated by the solvent. In addition, H_2O_2 formation rates in protic solvents are 10^3 larger than those measured in aprotic liquids and large kinetic isotope effects ($k_H/k_D > 7$) strongly suggest that alcohols serve as reactants in the kinetically relevant steps for H-$_2O_2$ formation. In parallel, O-O bonds within chemisorbed intermediates cleave to form H_2O with rates that are less sensitive to the solvent identity. Persistent organic surface residues introduce low barrier reaction pathways to reduce O_2* and increase those for O-O dissociation relative to reaction pathways in pure water. These results show that long-standing observations that H_2O_2 forms in greater yields within alcoholic solvent are not explained by simple differences in the solubility of H_2 in the liquid-phase. Similar rate laws and solvent requirements indicate that these reactions proceed by the same pathways in the presence of strongly binding halide adsorbates and acids. These modifications change barriers for the formation of H_2O (significantly) with lesser effects on barriers for steps that lead to H_2O_2, and are consistent with electronic modifications of Pd active sites by intra-atomic orbital rehybridization or by charge transfer from Pd atoms, respectively. Overall, this work presents evidence for the mechanism for H_2O_2 formation and explains the roles of solvent identity and surface modification strategies on H_2O_2 selectivities.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

SPM – Probing and Manipulating Nanoscale Structures

Moderators: Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA1 Building Artificial Quantum Matter with Dopant Atoms*, Sven Rogge*,** University of New South Wales, Australia **INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a “semiconductor vacuum” for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction*, Jeremy Schultz*,** *P. Whiteman, N. Jiang,* University of Illinois at Chicago

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthrequinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM*, Songbin Cui,*** Pohang University of Science and Technology, Republic of Korea*; U. Ham,* Institute for Basic Science (IBS), Republic of Korea*; T.-H. Kim,* Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the shaper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

[1] R. Zhang et al., Nature 498, 82–86 (2013).

[2] Z. C. Dong et al., Nature Photonics 4, 50–54 (2010).

[3] J. Aizpurua et al., Physical Review B 62, 2065-2073 (2000).

4:20pm **NS+AM+MI+MN+SS+TR-TuA7 Advances in SPM Methods for Energy-relevant Materials*, Marina Leite,*** University of Maryland College Park **INVITED**

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group's recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage Voc > 300 mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the Voc in perovskite solar cells with spatial resolution < 100 nm. Unexpectedly, we identify a 'residual Voc' post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

[1] *ACS Energy Letters* **2**, 2761 (2017). Invited Review.

[2]*ACS Energy Letters* **2**, 1825 (2017). Invited Perspective

[3] *Nano Letters***17**, 2554 (2017).

[4] *ACS Energy Letters***1**, 899 (2016).

[5] *Advanced Energy Materials* **5**, 1501142 (2015).

5:00pm **NS+AM+MI+MN+SS+TR-TuA9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon*, Chuanxu Ma,*** *L. Liang,* Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; A.A. Puretzky, K. Hong,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; A.-P. Li,* Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T') phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native sp^2 carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

5:20pm **NS+AM+MI+MN+SS+TR-TuA10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy*, MinHui Chang,*** Korea University, Republic of Korea*; Y.H. Chang, N.Y. Kim,* Korea Advanced Institute of Science and Technology (KAIST)*; U.S. Jeon, H. Kim,* Korea University, Republic of Korea*; Y.-H. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; S.-J. Kahng,* Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers*, Dominic Goronzy*[1]**, *E. Avery, N.M. Gallup,* University of California, Los Angeles*; J. Staněk, J. Macháček, T. Baše,* Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic*; K.N. Houk,* Chemistry and Biochemistry, University of California, Los Angeles*; P.S. Weiss,* University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers *via* STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied

---

[1] **NSTD Student Award Finalist**

contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a pK$_a$ of 3-3.2 in solution (3D) to an apparent surface pK$_a$ of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in pK$_a$ consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the pK$_a$ shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

Moderators: Jeffrey Fenton, Medtronic, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications***, **Andreas Thissen**, P. Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjaervik, W.E.S. Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

ACKNOWLEDGEMENTS: This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo***, **Jeffrey Fenton**, B. Theilacker, A. Belu, B. Tischendorf,* Medtronic **INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes***, R. Mom, L. Frevel,* Fritz-Haber Institute of the Max Planck Society, Germany*; J.J. Velasco-Velez,* MPI CEC Mülheim, Germany*; T.E. Jones, M. Plodinec,* Fritz-Haber Institute of the Max Planck Society, Germany*; R. Schlögl,* MPI CEC Mülheim, Germany*; **Axel Knop-Gericke**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a “non-innocent ligand”, but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***, Gabor A. Somorjai,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; “free OH^-”, liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface***, Takehiro Tamaoka, H. Yoshida, S. Takeda,* Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well–known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge–shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface***, Angela Silski, J. Petersen,* University of Notre Dame*; R.D. Brown,* Clarkson University*; S. Corcelli, S.A. Kandel,* University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

Plasma Science and Technology Division
Room 104A - Session PS+EM+NS+SS-TuA

Plasma Processing of Challenging Materials - II

Moderators: Michael Gordon, University of California at Santa Barbara, Wei Tian, Applied Materials Inc.

2:20pm **PS+EM+NS+SS-TuA1 Self-limiting Growth of III-nitride Materials via Hollow-cathode Plasma-ALD: Structural and Chemical Analysis***, Necmi Biyikli, A. Mohammad, D. Shukla,* University of Connecticut **INVITED**

Plasma-assisted/enhanced atomic layer deposition (PALD) provides an alternative route for the low-temperature synthesis of III-nitride thin films with sub-monolayer precision thickness control, ultimate three-dimensional conformality, and large-area uniformity. On the other hand, PALD synthesis of AlN, GaN, and InN films required relatively long plasma co-reactant exposure durations (40 - 120 sec) to achieve self-limiting surface saturation with minimal carbon impurities which directly correlates the effectiveness of the ligand-removal process. During such extensive plasma half-cycles, the plasma source itself is exposed to elevated temperatures and along with energetic hydrogen radicals, which resulted in etching of conventional quartz-based inductively coupled plasma (ICP) sources. We have mitigated this problem by using a stainless-steel based capacitively-coupled hollow-cathode plasma (HCP) source, which reduced the oxygen impurity levels at least two orders of magnitude in GaN films while increasing the average film grain/crystallite size of AlN films by one order of magnitude.

Using HCP-assisted ALD (HCP-ALD), we have grown the entire III-nitride wide bandgap semiconductor family (AlN, GaN, InN) at ≤200°C substrate temperatures with single-phase hexagonal poly-crystalline material quality. However, there is still plenty of room and need for improvement in material properties before we can use these layers as active device layers. A careful systematic study needs to be carried out to achieve device quality III-nitride films via HCP-ALD. In this talk, we will present an overview of our HCP-ALD efforts including our recent materials characterization results obtained with a custom-design HCP-ALD reactor. A particular focus will be devoted to the structural and chemical properties of the III-nitride films and how they correlate with reactor parameters and plasma conditions.

3:00pm **PS+EM+NS+SS-TuA3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor**, ***Tae Hwan Kim***, *SW. Lee,* National Fusion Research Institute, Republic of Korea

Plasma-liquid interaction research has increased because of emerging technological applications such as material synthesis, plasma bio-applications, environmental applications, and agriculture/food applications. Recently, an important scientific breakthrough in the understanding of the liquid reaction at the plasma-liquid interface that an electron transfer reaction at the plasma-liquid interface that leads to electrochemical reactions, which is referred to as the plasma electrochemical reaction [1]. Further evidence of plasma electron reaction (PER) was observed that the electrons in plasma can be solvated in a plasma electrochemical system [2].

In this talk, we present a new reaction pathway in which plasma-liquid interaction can cause an electrostatic charge in a liquid and the electrostatically charged solution can produce an electrochemical reaction. The experiments were performed with our newly designed plasma-coupled-microreactor (PCM), which can control the ambient gas and initiate a rapid plasma electrochemical reaction. Helium(He)-droplets and liquid-droplets were formed, and microplasma-droplets were ignited by dielectric barrier discharge (DBD). The generated microplasma-droplet can induce not only PER but also an electrostatic charge in a solution. The charge of the solution by microplasma-droplet and liquid-droplet interaction can be affected by the type and amount of stabilizer, the acidity of the solution, and the length of the electrodes used to form microplasma-droplets.

[1] C. Richmonds, M. Witzke, B. Bartling, S. W. Lee, J. Wainright, C. Liu, R. Mohan Sankaran, Electron-Transfer Reactions at the Plasma-Liquid Interface. J. Am. Chem. Soc. 133, 17582-17585 (2011)

[2] P. Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go, The solvation of electrons by an atmospheric-pressure plasma. Nat. Commun. 6, 7248 (2015).

3:20pm **PS+EM+NS+SS-TuA4 Surfactant-free and Stable Colloidal Metal Oxide Ultra-small Quantum Dots via Plasma-liquid Electrochemistry**, ***Dillibabu Padmanaban***, *D. Carolan, R. McGlynn, T. Velusamy, P. Maguire, D. Mariotti,* Nanotechnology & Integrated Bio-Engineering Centre, Ulster University, UK

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future. For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor. We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.

4:20pm **PS+EM+NS+SS-TuA7 From Organometallic Precursors to Bimetallic Nanocatalysts using Atmospheric-pressure Plasma Processes**, ***Joffrey Baneton***, *J. Mertens, M. Smiljanic, S. Cauchies, T. Segato,* Université Libre de Bruxelles, Belgium*; Y. Busby,* Université de Namur, Belgium*; G. Caldarella,* Université de Liège, Belgium*; V. Debaille, S. Godet,* Université Libre de Bruxelles, Belgium*; J.-J. Pireaux,* Université de Namur, Belgium*; N. Job,* Université de Liège, Belgium*; M.J. Gordon,* University of California at Santa Barbara*; R.M. Sankaran,* Case Western Reserve University*; F. Reniers,* Université Libre de Bruxelles, Belgium

Developing new technologies to produce energy while respecting the environment is one of the important challenges in materials science. One of the possible routes is the use of hydrogen fuel cells. Unfortunately, some limitations remain such as the electrocatalysis of the reduction of dioxygen which requires a rare and expensive metal: platinum [1]. Therefore, minimizing its amount at the cathode while maximizing its accessibility, electroactivity and stability constitutes one of the main goal of current research. An interesting way consists in the synthesis of platinum-based alloys. Indeed, it is well known in the literature that combining two metals leads to the production of durable materials with higher activity [2].

Different routes can lead to the formation of bimetallic nanostructures including wet-chemistry, ultrasound processes or thermal evaporation. In this catalogue of methods, atmospheric-pressure plasma techniques are very attractive due to their versatility, rapidity and ease of use. In the present research, two different kinds of reactors, a microplasma device [3] and radio-frequency plasma torch [4], have been used to study the synthesis of bimetallic nanoparticles from acetylacetonate precursors. A complete chemical and morphological characterization is provided thanks to the combined use of X-ray photoelectron spectroscopy, transmission electron microscopy, UV-visible spectroscopy and X-ray crystallography.

Different experimental parameters can play a crucial role is the reduction process of the organometallic precursors. For example, concerning the microplasma system, the initial concentrations have a direct influence on the size distribution and agglomeration while, concerning the RF plasma torch treatment, the nature of the plasma gas mixture can limit the production of nanoparticles or favor their anchoring at the surface of a carbon support [5]. After optimization of the processes, electrochemical measurements were conducted to evaluate their activity, stability and performances as catalysts for hydrogen fuel cells.

The authors would like to thank the Walloon Region (HYLIFE project n°1410135, Energinsere program) for the financial support.

[1] F. Maillard et al. In: Carbon materials for catalysis (**2009**), 429-480.

[2] Z. Li et al. Int. J. of Hydrogen Energy (**2012**), 37, 14152–14160.

[3] C. De Vos et al. J. Phys. D: Appl. Phys. (**2017**), 50, 105206.

[4] D. Merche et al. Plasma Process. Polym. (**2016**), 13, 91–104.

[5] A. Felten et al. J. Phys. D: Appl. Phys. (**2007**), 40, 7379.

4:40pm **PS+EM+NS+SS-TuA8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH_4+Ar Plasmas and Their Deposition**, ***Kazunori Koga***, *S.H. Hwang, K. Kamataki, N. Itagaki,* Kyushu University, Japan*; T. Nakatani,* Okayama University of Science, Japan*; M. Shiratani,* Kyushu University, Japan

Nanostructure fabrication such as nanoparticles through bottom-up processes is important in nanotechnologies due to their size-related properties [1]. Plasma is a powerful tool to produce nanoparticles. To control their size, pulsed discharge plasmas are commonly employed, but the plasmas have the limitation of the throughput. To realize continuous production, we have developed a multi-hollow discharge plasma chemical vapor deposition (MHDPCVD) method. We have succeeded in producing crystalline Si nanoparticles of 2 nm in size using hydrogen diluted silane plasmas [2, 3]. Here we applied the method to synthesis carbon nanoparticles. The experiments are carried out by CH_4+Ar MHDPCVD. CH_4 and Ar were injected into the reactor, flowed through hollows of 5 mm in diameter in the electrode. The gas flow rate ratio of CH_4 and Ar was 1:6. The total gas flow rate was 10 to 200 sccm . The pressure was kept at 2 Torr. Discharges were generated in hollows by applying rf power of 40 W at 13.56 MHz. Nanoparticles are nucleated and grow in the discharges. They are transported outside of the discharges by the fast gas flow and the growth of the nanoparticles are stopped. They deposited on TEM mesh grids set on the substrate holder 50 mm far from the electrode. From TEM measurements, spherical nanoparticles were deposited on the grid. The mean size decreases from 270 nm for 10 sccm to 20 nm for 120 sccm . The gas residence time for 120 sccm is 1/12 of that for 10 sccm . The size for 120 sccm is 1/13.5 of that for 10 sccm . The results indicate that the size of carbon nanoparticles are controlled by gas residence time of nanoparticles in plasmas. Above 125 sccm, No nanoparticle is observed on the TEM mesh. It suggests that deposition of nanoparticles depends on gas flow velocity and direction on the substrate.

[1] M. Shiratani, et al., J. Phys. D 44 (2011) 174038.

[2] T. Kakeya, et al., Thin Solid Films 506 (2006) 288.

[3] K. Koga et al., ECS Transactions 77 (2017) 17.

5:00pm **PS+EM+NS+SS-TuA9 Antimony-doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma**, ***Qinyi Chen***, *E. Thimsen,* Washington University in St. Louis

For electrochemical applications, metal-oxide materials are attractive as electrodes for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area. Among conductive metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high chemical stability over a wide range of pH values and reduction potentials, 2) high electrical conductivity, and 3) abundant constituent elements. Synthesis of ATO nanocrystals has been developed in liquid phase using sol-gel and colloidal methods. However, post-synthesis heat treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and pore structure of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. The precursor vapors reacted to nucleate ATO nanocrystals. Thin films comprised of ATO nanocrystals were then immediately deposited by supersonic impact deposition of the aerosol resulting from plasma synthesis. The resulting materials were characterized by a variety of methods to determine film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were assessed by Fourier-transform infrared absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation. The effects of nanocrystal size on the transport properties of ATO thin films will be presented.

5:20pm **PS+EM+NS+SS-TuA10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN**, ***Chisung Ahn***, *E. Barlaz, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Pulsed femtosecond lasers have been used as a functionalization method for metal surfaces due to their ability to produce nanostructures uniformly with easily controlled user inputs such as spot size and exposure repetition. Laser assisted nitriding of Ti in ambient nitrogen has previously been demonstrated in our group to significantly reduce native oxides. A major challenge to the current process is the limited ability of the laser to produce nitrogen radicals.

In this study, we investigate the effects of increased nitrogen radical concentration on surface topography and chemical composition for textured Ti metal. A secondary DC plasma is generated along the path length of the laser close to the sample surface in ambient nitrogen and under vacuum. The surface topography and chemical compositions of the resultant Ti coupons are analyzed by SEM and XPS respectively. Changes to hydrophilicity are quantified using contact angle measurements.

5:40pm **PS+EM+NS+SS-TuA11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis**, ***Bocong Zheng***, *M. Shrestha, K.L. Wang, T. Schuelke, Q.H. Fan,* Michigan State University

Contact glow discharge electrolysis is becoming attractive for nanomaterials manufacturing and surface engineering. In this discharge electrolysis, an electrode is submerged in a liquid electrolyte and a plasma is formed in a vapor layer around the electrode. The process combines the characteristics of electrolysis and plasma discharges, creating high-energy-density plasmas that lead to intensive physical processes and chemical reactions on the working electrode. The authors have found that the physical processes and the chemical reactions could be decoupled under certain conditions. In that case, a textured electrode surface could be created through a chemical-reaction-dominated process instead of an irregular porous surface produced by the physical-reaction-dominated interactions. The mechanisms are not clearly understood yet. This study aims to elucidate the plasma characteristics and the chemical reactions in contact glow plasma electrolysis. A plasma fluid model is established to predict the discharge process with constraint conditions obtained from the experiments. The modeling reveals that the plasma is highly electronegative, and the dominant neutral species are H_2 and O_2 dissociated from water vapor. The formation of textured surface is attributed to the anisotropic chemical etching by the reactive species generated in the plasmas.

6:00pm **PS+EM+NS+SS-TuA12 Effects of Light Ion Beam Irradiation in Plasma Etching Processes**, ***Kazuhiro Karahashi***, *T. Ito, H. Li, M. Isobe, K. Mizotani, S. Shigeno,* Osaka University, Japan*; M. Fukasawa, A. Hirata, T. Tatsumi,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguch,* Osaka University, Japan

Gases containing hydrogen are widely used in microfabrication processes of electronic devices using plasma etching. For example, HBr gas is used for silicon etching, hydrofluorocarbon gases are used for silicon oxide etching, and Hydrocarbon-based non-corrosive gases are used for transparent conducing oxides etching. Unlike other atoms, hydrogen is lighter in weight, smaller in atomic radius, and chemically reactive, so it has various effects in the etching process. In order to precisely control the etching reaction and realize nanometer order microfabrication processes, it is necessary to clarify the effect of hydrogen. In this study, by comparing various effects on etching processes between hydrogen and helium incident ions using molecular dynamics (MD) simulation and ion beam experiments, physical and chemical effects by such light ion injection on etching processes were evaluated.

We have shown in this study based on MD simulation and ion beam experiments that, when a Si surface exposed to an O radical flux is simultaneously irradiated by an H^+ or He^+ ion beam, diffusion of oxygen atoms into the Si film is promoted. Since the enhanced diffusion occurs in a similar manner in both cases of H^+ and He^+ ion injections, it is clear that the enhanced diffusion is essentially caused by knock-on effects by incident light ions. On the other hand, in the case of etching of ZnO, which is an ionic crystal, our beam experiments have shown that its crystal size decreases by light ion irradiation using in-plane X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) measurements. The reduction of grain sizes seems correlated with the reduction of the physical sputtering yield of the ZnO film.

The results above show the following two physical effects by irradiation of a substrate with light ions such as H^+ and He^+ ;1) enhancement of diffusion of heavy atoms deposited on the substrate surface into it's the bulk of the film and 2) decrease of grain sized of ionic crystalline substrate due to amorphization and recrystallization. The decrease of grain sizes, which induce the increase in grain boundary areas may contribute to an increase in sputtering yield of the substrate.

Surface Science Division
Room 203C - Session SS+HC+MI-TuA

Oxides/Chalcogenides: Structures and Reactions

Moderator: Andrew Teplyakov, University of Delaware

2:20pm **SS+HC+MI-TuA1 New Eyes for Nanocatalysis: Atomic Scale Investigations of TiO_2 Chemistry**, ***Melissa Hines,*** Cornell University **INVITED**

The atomic-scale surface chemistry of nanocatalysis has remained relatively unexplored for two simple reasons. First, nanocatalysts are too small to be studied individually with most surface science techniques. Second, nanocatalysts are typically used at ambient pressure or in solution — conditions where surface contamination is a significant concern. In this talk, I will review our work in developing "new eyes for nanocatalysts" that address both issues.

Addressing the issue of size, I will show that hydrothermal crystal growth techniques can produce anatase nanocrystals suitable for study at the atomic-scale with STM and a panoply of techniques. Despite being synthesized in solution, the nanocrystal surfaces are very clean and passivated by a protecting monolayer. Using these crystals, I will show that the most commonly used functionalization chemistry for oxide nanocatalysts, a carboxylic acid solution, causes the spontaneous reorganization of the nanocatalyst, leading to *a five-fold increase in the number of reactive sites.*

Addressing the issue of contamination, I will explain the chemical origin of the molecularly ordered interfaces that have been observed by researchers around the world when TiO_2 surfaces are exposed to air or solution. Although these structures have recently been attributed to a new (2 × 1) ordered state of adsorbed H_2O, we show that clean TiO_2 surfaces selectively adsorbs atmospheric organic acids that are typically present in parts-per-billion concentrations while effectively repelling other adsorbates, such as alcohols, present in much higher concentrations. This finding may have important implications for TiO_2 photocatalysis, as the self-assembled carboxylate monolayer resists desorption under environmental conditions while effectively blocking the transition metal sites typically implicated in photocatalysis.

As time allows, I will also show that solution-phase techniques can be used to prepare a wide variety near-atomically-perfect, self-assembled monolayers on TiO_2 surfaces.

3:00pm **SS+HC+MI-TuA3 Coverage-dependent Water Agglomerates on Fe_3O_4 Surfaces***, **Zdenek Jakub,*** Vienna University of Technology, Austria*; M. Meier,* University of Vienna, Austria*; J. Hulva, J. Pavelec, M. Setvin, M. Schmid, U. Diebold,* Vienna University of Technology, Austria*; C. Franchini,* University of Vienna, Austria*; G.S. Parkinson,* Vienna University of Technology, Austria

The interaction between iron oxides and water plays a key role in many natural and technological processes. Recent water adsorption studies have found significant complexity on metal oxides, with reports of mixed-mode adsorption and hydrogen bonding. Here we present a multi-technique study of water adsorption on Fe_3O_4 surfaces. Utilizing quantitative temperature programed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS), we identify four partially dissociated phases in the submonolayer regime on the Fe_3O_4(001), corresponding to coverages of 9, 8, 6 and 3 molecules per surface unit cell. These are investigated by non-contact atomic force microscopy (nc-AFM) with tip functionalized by CO molecule, and the observed structures are further interpreted by DFT-based calculations. We clearly demonstrate the existence of partially dissociated dimers and trimers at lower coverage, and a build-up of complex hydrogen-bonded network with increasing coverage. Applying the same approach on the Fe_3O_4(111) we discuss the general trends of water adsorption on Fe_3O_4 surfaces.

3:20pm **SS+HC+MI-TuA4 Reversible Structural Evolution and Identification of the Catalytically Active Phase of $NiCoO_xH_y$ During the Oxygen Evolution Reaction (OER)***, **Bruce E. Koel,*** Princeton University

Significant improvements in the activity of transition metal oxides (TMOs) for the oxygen evolution reaction (OER) have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, and using conductive supports. However, the complex composition and structure of TMO catalysts have hindered the elucidation of clear structure-activity correlations. We have utilized a range of electrochemical techniques, such as electrical impedence spectroscopy (EIS), and spectroscopic techniques, including ambient pressure photoelectron spectroscopy (APPES), for characterization of pure and Ni-modified cobalt (oxy)hydroxide electrocatalysts for OER. In particular, operando Raman spectroscopy and electrochemical techniques were used during the oxygen evolution reaction to identify the composition and local structure of electrodeposited CoO_xH_y and $NiCoO_xH_y$ catalyst films. In these studies, several unique initial catalyst structures and crystallinities were prepared by subjecting the samples to a variety of thermal and electrochemical conditioning procedures before evaluation. During oxygen evolution, Ni-modified CoO_xH_y films with lower initial crystallinity underwent substantial structural evolution that began with an irreversible transformation of a spinel local structure to an amorphous CoO structure at low anodic potentials. Increasing anodic polarization with elevated oxygen evolution rates caused additional structural conversion of the amorphous CoO structure to a complex phase that can be described as an amalgamation of NiOOH and layered CoO_2 motifs (NiOOH-h-CoO_2). The formation of this active structure was correlated with improved OER activity. Formation during oxygen evolution of the same NiOOH-h-CoO_2 structure independent of the initial cobalt oxide structure suggests that this active phase identified in these studies could be the universally active structure for $NiCoO_xH_y$ catalysts.

4:20pm **SS+HC+MI-TuA7 Understanding the Growth and Chemical Activity of Titania-Supported MoS_x Clusters***, **Donna Chen,*** University of South Carolina*; R.P. Galhenage,* University of California at Irvine*; H. Yan,* University of Louisiana Layfette*; D. Le, T.B. Rawal, T.S. Rahman,* University of Central Florida

MoS_x clusters have been grown on TiO_2(110) in order to provide a model surface for better understanding adsorbate interactions and chemical activity of supported MoS_x clusters; MoS_2 particles have exhibited excellent catalytic activity for a variety of reactions, particularly for hydrodesulfurization and photocatalysis, and interactions with the support are believed to induce new electronic properties. The MoS_x clusters were grown by deposition of Mo on titania in an atmosphere of H_2S, followed by annealing to 950 K in H_2S. Scanning tunneling microscopy experiments show that clusters with elongated, rectangular shapes and flat tops are formed, and the long axes of the clusters have specific orientations with respect to the [001] direction on TiO_2(110). In contrast, deposition of Mo in the absence of H_2S results in a high density of smaller, round clusters that cover the majority of the surface. The morphologies of MoS_x clusters do not change after exposure to various gases (D_2, CO, O_2, methanol) in ultrahigh vacuum. However, exposure to higher pressures of O_2 (250 mTorr) or air causes the clusters to disintegrate as Mo in the clusters becomes oxidized. Temperature programmed desorption studies with CO on the MoS_x clusters show a distinct desorption peak at 275 K, which is not observed on metallic Mo or titania. Density functional theory calculations demonstrate that the presence of the titania support changes in the favored adsorption site for CO from the (-1010) edge in the pristine MoS_2 to the (10-10) edge for the supported MoS_2. Furthermore, the MoS_x/TiO_2(110) interfacial sites are not favored for CO adsorption.

*This work is partially supported by DOE grant DE-FG02-07ER15842.

4:40pm **SS+HC+MI-TuA8 Analyzing Single Atom Catalysts using Low Energy Ion Scattering (LEIS)***, **Thomas Grehl,*** IONTOF GmbH, Germany*; R. ter Veen,* Tascon GmbH, Germany*; D. Kunwar, A. Datye,* University of New Mexico*; H.H. Brongersma,* IONTOF GmbH and Tascon GmbH, Germany

An important goal of heterogeneous catalyst synthesis is the dispersion of the active metal uniformly on a catalyst support, ideally achieving atomic dispersion. Isolated atoms dispersed on oxide supports (single-atom catalysts) provide efficient utilization of scarce platinum group metals, and higher reactivity as well as better selectivity for a range of catalytic reactions.

One of the challenges is to achieve high enough loadings and to prevent agglomeration by limiting the synthesis and operation temperature. Consequently, the characterization of these materials is essential to monitor the dispersion.

Low Energy Ion Scattering (LEIS) is a surface analytical technique that quantitatively determines the elemental composition of the outer atoms with ultimate surface sensitivity. LEIS is compatible with non-conducting supports and insensitive to topography, making it an ideal tool to analyze both model and industrial catalysts. Due to its unique surface sensitivity the results of the analysis usually correlate directly with the properties of the catalyst.

This contribution demonstrates the analysis of Pt/CeO_2 single atom catalysts using LEIS. During synthesis (atom trapping) the Pt precursor is heated in air at 800 C to form mobile Pt species that deposit on the support and are strongly bound. On high surface area ceria, metal loadings of 3 wt. % can be achieved while maintaining almost exclusively single atoms. We will describe how LEIS was essential to demonstrating the single atom nature of the catalyst. In conjunction with X-ray absorption spectroscopy (XAS), Aberration-Corrected Scanning TEM (AC-STEM) and Diffuse Reflectance Infrared Absorption Spectroscopy (DRIFTS) we were able to develop an accurate picture of the sites that bind Pt ions on the support. The atomistic model for the single atom Pt catalyst was corroborated by Density Functional Theory (DFT).

The LEIS results revealed that with increasing metal loading, the fraction of Pt visible to LEIS decreased by 20%. However XAS, DRIFTS and AC-STEM confirmed that the Pt was present in single atom form even at the highest metal loadings. Further analysis led to the realization that the Pt atoms are present in close proximity at high loadings, causing some of the Pt to be rendered invisible to LEIS. The loss in LEIS signal could be correlated with the differences in reactivity for CO oxidation, which otherwise could not be easily explained. This application demonstrates the extreme sensitivity of LEIS which makes this analytical approach essential for study of heterogeneous catalysts used in industry.

Part of this work was supported by DOE grant DE-FG02-05ER15712 and NSF grant EEC-1647722.

5:00pm **SS+HC+MI-TuA9 Synthesis and Characterization of Metals Supported on ZnO Nanoparticles***, **Amanda Haines**, D.F. Ferrah, J.C. Hemminger,* University of California at Irvine

Various metals on transition metal oxide supports, such as Cu/ZnO, have been widely studied to understand their role in CO_2 hydrogenation. However, there still remains a dispute as to the role of the oxide supports and the surface oxidation state of the active metal and its efficacy in the reduction of CO_2, namely on the nature of CO_2 adsorption and activation. Here, we have designed and characterized a model catalytic system that will enable us to explore the chemistry of various metals (M_i: i=Pt,Cu) on ZnO supports. ZnO nanoparticles (NPs) have been deposited on an inert highly oriented pyrolytic graphite (HOPG) substrate by physical vapor deposition (PVD). From scanning electron microscopy (SEM), we have seen that hexagonal shaped ZnO nanoparticles are formed on a defect-free HOPG substrate. Different surface plasma treatments have been explored to create defect sites on the HOPG substrate to better control the density of the ZnO NPs and various substrate temperatures have been studied to investigate its effect on the size, morphology, structure and chemistry of the NP growth process. Different metals, Pt and Cu, are photodeposited on the ZnO NPs and fully characterized using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature programmed desorption (TPD) to gain fundamental information about the oxidation states and active sites of these M_i/ZnO NPs. Future work will involve reactivity studies on the fully characterized M_i/ZnO NPs using ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) to investigate the surface chemistry, intermediates and products of this catalyst to gain insight into the reaction mechanism of CO_2 hydrogenation.

5:20pm **SS+HC+MI-TuA10 Molecular Water Adsorption and Reactions on α-Al_2O_3(0001) and α-Alumina Particles***, **Greg Kimmel**, N.G. Petrik,* Pacific Northwest National Laboratory*; P.L. Huestis, J.A. LaVerne,* University of Notre Dame*; A.B. Aleksandrov, T.M. Orlando,* Georgia Institute of Technology

Alumina and its interactions with water are important in areas ranging from electronics and catalysis to environmental science. However, a basic understanding of the adsorption and reactions of water on even the simplest alumina surface, the (0001) surface of α-alumina, remains elusive. We have investigated the adsorption and reaction of water on single crystal, α-Al_2O_3(0001) in ultrahigh vacuum, and α-alumina particles in ambient conditions, using temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and other surface science techniques. For a water coverages of 1 and 2 H_2O/(surface Al^{3+}) on α-Al-$_2O_3$(0001), no evidence for the surface hydroxyls expected from dissociative adsorption was observed, while the v_2 vibration of molecular water was observed. Electron-stimulated desorption of molecular water at low coverages also indicated molecular or mixed (molecular plus dissociative) adsorption. In contrast with the single crystal results, IR spectra of water adsorption on alumina particles indicated the presence of surface hydroxyls that persist even after annealing to high temperatures in oxygen. The results, which are consistent with at most a small amount of water dissociation on the Al-terminated (0001) surface, are difficult to reconcile with calculations suggesting that the barrier to dissociation is small. However, the results are consistent with recent vibrational sum frequency experiments showing that the hydroxylation of the Al-terminated (0001) surface takes many days even at ambient pressures and temperatures.

5:40pm **SS+HC+MI-TuA11 Applying Low Temperature Titration for Determination of Metallic Sites on Active Oxide Supported Catalysts***, **Jerry Pui Ho Li**, Z. Liu, Y. Yang,* ShanghaiTech University, China

Catalysts are used in a variety of applications from the production of fuels or consumer chemicals, and the environment. Characterization of such catalysts is critical, since it allows for an accurate representation of its effectiveness. For optimum design and efficient utilization of catalysts, it is important to be able to connect model catalyst and industrial catalyst turnover frequencies (TOF) based on the same benchmark for active sites, such as metallic sites, for catalyst evaluation and further kinetics studies. Characterization of the active sites with chemisorption is ideally performed with high time resolution and sensitivity; particularly for catalysts with low loading of the active particles.

Chemisorption study is the common method for active site determination, but has limitations for active heterogeneous catalysts; particularly industrial catalysts because the method often cannot distinguish the redox on metallic sites and catalyst support. An online micro reactor combined with online mass spectroscopy was developed for kinetics studies within wide temperature (as low as liquid nitrogen) and pressure ranges. Pt and Cu based catalysts are used as demonstration of this technique for metallic sites quantitative calibration in this study. Pt catalysts were characterized using CO oxidation and Cu catalysts were characterized using N_2O decomposition. By comparing titration products curves (CO_2 for Pt catalysts, and N_2 for Cu catalysts) versus temperature for both supported samples, narrow subzero temperature windows are found for each catalyst, demonstrating that the titration products are only related with metallic sites. Pure metallic powder was analyzed for confirmation. Specialized chemisorption procedure was established for each sample. This procedure shows a reliable direct titration measurement recipe for the characterization of supported catalysts, quantifying only the metallic sites for catalysts while being selective against surfaces that contribute secondary reactions often found with more complex supports.

We also present a specialized chemisorption technique applied for metallic sites determination of Au nanoparticles on TiO_2 support through CO at low temperature by comparing IR assignment.

6:00pm **SS+HC+MI-TuA12 Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures***, **Shanyuan Niu**,* University of Southern California*; G. Joe,* University of Wisconsin - Madison*; H. Zhao, M. Mecklenburg,* University of Southern California*; T. Tiwald,* J.A. Woollam Co. Inc*; K. Mahalingam,* Air Force Research Laboratory*; H. Wang,* University of Southern California*; M. Kats,* University of Wisconsin - Madison*; J. Ravichandran,* University of Southern California

Optical anisotropyis a crucial building block to engineer the polarization of light in polarizing optics, light modulators, imaging and communication systems. While metamaterial architectures with form birefringence can overcome the limited optical anisotropy available in widely used natural anisotropic crystals, their deployment is limited by the demanding fabrication. We demonstrate the realization of giant optical anisotropy via chemically engineering the polarizability tensor in a natural material, $BaTiS_3$, which has a highly anisotropic quasi-1D structure and features easily accessible in-plane anisotropy. Large single crystals were grown with the chemical vapor transport method. We report the observation of a large, broadband infrared birefringence and linear dichroism. As-grown crystals demonstrate strong dichroism with two distinct optical absorption edges for light with polarizations along two principal axes. To our knowledge, the unprecedented birefringence in the transparent region is more than twice as large as that in any other bulk crystal.

Thin Films Division
Room 102A - Session TF+SS-TuA
Organic/Inorganic Materials and Interfaces

Moderator: Matthew Richard Linford, Brigham Young University

2:20pm **TF+SS-TuA1 Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Organic/Inorganic Systems***, **Sven Pletincx**,* Vrije Universiteit Brussel, Belgium*; L. Trotochaud,* Lawrence Berkeley Lab, University of California, Berkeley*; L.-L. Fockaert, M. Meeusen, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Bluhm,* Lawrence Berkeley Lab, University of California, Berkeley*; H. Terryn, T. Hauffman,* Vrije Universiteit Brussel, Belgium

The durability of hybrid systems is mainly determined by the different phenomena occurring at the organic/inorganic interface. However, analyzing this solid/solid or liquid/solid interface under technologically relevant conditions is challenging. Recently, the *in situ* investigation of these so-called buried interfaces is done by monitoring ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).[1,2] Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of different acrylic coatings with aluminum oxide.

The deposition of this nanometer thin overlayer is often carried out by reactive adsorption from dilute polymer solutions. However, the influence of the solvent on the metal oxide chemistry is seldom taken into account in interface studies. An integrated spectroelectrochemical setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to monitor the influence of the solvent on the metal oxide surface. An aluminum layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the

Kretschmann effect, and a near-interface spectrum of the organic/oxide surface is obtained. The occurring interface processes can be followed with infrared spectroscopy while simultaneously, the PVD layer acts as a working electrode. This allows to determine the electrochemical properties of the overall hybrid system, studied by ORP-EIS.[3]

After the characterization of the solvent interactions, *in situ* ATR-FTIR Kretschmann/ORP-EIS is used to study the effect of an electrolyte on an acrylic polymer/metal oxide system. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. Also the study of covalent bonding, such as the interfacial interactions of silane adhesion promotors are investigated. This work shows that by using ultrathin films and a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.***7,** 45123 (2017).

2. Pletincx, S. *et al.* Unravelling the Chemical Influence of Water on the PMMA/Aluminum Oxide Hybrid Interface In Situ. *Sci. Rep.***7,** 13341 (2017).

3. Hauffman, T. *et al.* Measuring the adsorption of ethanol on aluminium oxides using odd random phase multisine electrochemical impedance spectroscopy. *Electrochem. commun.***22,** 124–127 (2012).

2:40pm **TF+SS-TuA2 Microscopic and Spectroscopic evidence of Odd-Even Effect in Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid on Ag(111)***, **Anna Krzykawska,*** Jagiellonian University, Polska*; P. Cyganik, M. Szwed, J. Ossowski,* Jagiellonian University, Poland

Self-assembled monolayers (SAMs) have been broadly studied as a model system for inorganic-organic interface in molecular electronics and biosensing devices. Current standard in SAMs formation is based on using sulfur as an anchoring group to the metal substrate. In our recent paper[1] we have indicated that by replacing thiol headgroup by carboxylic, a highly interesting alternative is obtained, particularly when 2D ordering, SAM fabrication time and stability in ambient conditions are of great importance. Following this first observation made for a specific system, in the current work we have investigated a homolog series of SAMs based on biphenyl-substituted fatty acids on Ag(111) in the form of $(C_6H_4)_2$-$(CH_2)_n$-COO/Ag (BP*n*COO/Ag, *n* = 1-4). The series of experiments were carried out using infrared reflection absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The results of this combined microscopic and spectroscopic analysis demonstrate very strong dependence of the structural properties on the number of the CH_2 groups in the short aliphatic linker. Monolayers with *n* = even show highly ordered and stable structures. In contrast, SAMs with *n* = *odd* have disordered liquid-like structure with more canted orientation of the molecular backbone and the carboxylic headgroup, which results in lower packing density and film thickness compared to the even-numbered SAMs. By comparing obtained results with former odd-even effects reported for analogues SAMs based on thiols and selenols[3,4], a common, qualitative model relating the odd-even effect to the monolayer stability and structure will be discussed. Our results demonstrate that for BP*n*COO/Ag, this odd-even effect is particularly strong and fully controls the ability of molecules to form highly ordered structures. This observation seems to be of key importance for the design of SAMs based on the carboxylic group, which, for correctly designed molecules, forms much better 2D-ordered structures compared to commonly used thiols.

References

[1] K rzykawska, A.; Ossowski, J.; Zaba, T.; Cyganik*, P., Chem. Comm. **2017**, *53*, 5748-5751

[2] Krzykawska, A.; Szwed, M.; Ossowski, J.; Cyganik*, P., J. Phys. Chem. C **2018**, *122*, 919-928

[3] Cyganik, P.; Buck, M.; Azzam, W.; Wöll*, C., J. Phys. Chem. B. **2004**, *108*, 4989-4996

[4] Cyganik*, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov,M., J. Phys. Chem. C. **2008**, *112*, 15466-15473

3:00pm **TF+SS-TuA3 CVD of Thin Polymer Films for Engineered Material Properties***, **AnnaMaria Coclite,*** Graz University of Technology, Austria **INVITED**

Functional thin films offer innovative solutions for many technological applications: organic electronics, smart devices for biotechnology, microfluidics, membrane technology, sensors and drug delivery systems. The development of functional thin films, engineered to achieve all the desired properties, requires advanced growth techniques. The development of dry growth methods - based on vacuum- aims to complement and enlarge the applicability of functional thin films to fields where the presence of solvent is detrimental.

Successful results in terms of rationally designed micro- and nanoengineered materials will be demonstrated using as a case of study the growth of functional polymers by initiated CVD (iCVD). The high versatility of iCVD in driving application-specific properties into the material, creating a platform for the implementation of polymeric coatings into device fabrication will be discussed.

Layered nanostructures in proton conductive iCVD polymers were investigated though X-ray based methods. The polymers crystallize in a bilayer structure, perpendicular to the substrate surface, formed by perfluorinated pendant chains. Acid moieties were introduced to form ionic channels among the bilayers –parallel to the substrate surface- which can be responsible for proton conduction. This one-step polymerization process has the potential to manufacture inexpensive, high quality membranes for proton exchange membrane fuel cells.

Another case of study will be presented in the field of multi-stimuli-responsive materials. In particular, the material of interest in this case is a hydrogel that changes its size and shape when stimulated by light and humidity. Hydrogels are known for their dynamic swelling response to aqueous environments. A chemical functionalization of the hydrogel surface was performed to add other stimuli-responsive functionalities and obtain a smart material that responds to two stimuli. Modifying the hydrogel surface with solution-based methods is often problematic because of the damages caused by the permeation of solvents in the hydrogel. This issue is completely bypassed by the use of solvent-free techniques, like iCVD.

4:20pm **TF+SS-TuA7 Organosilicon Functionally Nanostructured Films as Engineered Interlayers for Hybrid Materials***, **Vladimir Cech,*** Brno University of Technology, Czech Republic*; J. Houdkova,* Institute of Physics, Academy of Sciences of the Czech Republic*; M. Branecky, T. Plichta,* Brno University of Technology*; J. Zemek,* Institute of Physics, Academy of Sciences of the Czech Republic

Thin films of organosilicones synthetized in low-temperature plasma constitute a class of materials with a rich and varied scientific background. This class of materials in the form of hydrogenated amorphous carbon-silicon (a-CSi:H) films has a distinctive characteristic that distinguishes it from other thin films – the ability to vary and control the degree of organic/inorganic character and crosslinking of carbon-silicon network by appropriate choice of fabrication variables. Oxygen atoms can be incorporated in organosilicon film to form new chemical bonds (Si-O, C-O, C=O) and vary the mechanical properties of hydrogenated amorphous carbon-silicon oxide (a-CSiO:H) films by modifying the carbon-silicon network. However, a multilayer rather than single layer film can fulfill specific functions not only in sophisticated electronic, optical, mechanical, and biomedical devices, but also in hybrid materials (composites and nanocomposites) with controlled interphase.

Functional multilayer nanostructures with controlled distribution of mechanical properties across the nanostructure were constructed from oxygen-free (a-CSi:H) and oxygen-bound (a-CSiO:H) individual layers deposited at different effective power or pulse period from tetravinylsilane and tetravinylsilane in a mixture with oxygen gas, respectively, by plasma-enhanced chemical vapor deposition operated in pulsed mode. XPS depth profiling using argon cluster ion beams was used to determine the atomic concentration of carbon, silicon, and oxygen in individual layers forming the multilayer nanostructures with a total thickness of about 100 nm. The XPS analysis revealed that the oxygen-free layers were oxidized due to post-deposition oxidation in the ambient air. Oxygen was even diffused in an oxygen-bound layer, which was confirmed by repeated XPS depth profiling within three months after multilayer deposition. The upper oxygen-bound layer at the multilayer surface behaved as a barrier reducing oxygen diffusion. The high energy-resolution XPS spectra (C 1s, Si 2p, and O 1s) were analyzed to gain more insight into bonding species formed in functionally nanostructured film. This detailed analysis showed that oxygen atoms, originating from the ambient air, were bound in oxidized (a-CSi:H) layers forming the same bonding states as those in as-deposited oxygen-bound layers.

4:40pm **TF+SS-TuA8 Studying Electron Induced Chemical Changes of Hafnium Oxide-Methacrylate EUV Photoresists with *In Situ* IR Spectroscopy and Model Flat Surfaces***, **Yasiel Cabrera**, E. Mattson, K. Oyekan, Y. Wang, Y.J. Chabal,* University of Texas at Dallas

New development in extreme ultraviolet (EUV) photolithography, using 13.5 nm photons, has brought us closer to a new era of device fabrication with sub-10 nm nodes. In the last decade, there has been many significant contributions to the development of EUV lithography, but limitations in photoresist development has made it difficult to implement the technology. Another significant challenge arises from the reality that EUV scanners are very expensive and limited for academia purposes, which ultimately slow down the process in understanding important mechanistic details for optimization of EUV resist materials. In this work, we emulate industrial EUV ionizing photons/events with low energy 90 eV electrons, which are believed responsible for inducing chemistry. Here, we are presenting results for nanoclusters resist based on hafnium-oxide core capped with methacrylic acid ligands (HfMAA). Using a combination of *in situ* infrared (IR) spectroscopy and density functional theory (DFT) calculations, we establish an atomic-scale mechanistic picture for each step of a photo-lithography process. To further understand the chemical changes leading to solubility switching, we have also developed a model surface system by translating the 3D structure considered in an HfMAA thin films (< 30 nm thick on SiO_2) to a 2D system comprised of a single methacrylic acid (MAA) monolayer grafted onto an ALD grown HfO_2 film. The model system allows us to explore three areas related to the nanocluster system: first IR spectroscopy shows that the model surface is a good representation of the HfMAA thin film by matching many of the IR modes observed; second, similar to HfMAA, 90 eV electron irradiation shows the formation of alkyl CH_2 groups on the surface, with the loss of carboxylate and C=C bonds in the MAA adlayer; third, by comparing with different metal-oxide surface (Al_2O_3 and TiO_2) and different carboxylate ligands (isobutyric acid (IBA), and hydroxybenzoic acid (OHBA)), we have demonstrated that analogous metal oxide/adlayer combinations can be used as a comparative tool to survey optimal combinations of organic and inorganic compounds for resist development by quantitatively evaluating the role of metal centers in inducing reactions.

5:00pm **TF+SS-TuA9 Photoactivated Molecular Layer Deposition of Fluoropolymer Thin Films***, **Richard Closser**,* Stanford University*; M. Lillethorup,* Radisurf Aps, Denmark*; D.S. Bergsman, J. Shi, S.F. Bent,* Stanford University

Recent developments of organic thin-film technologies have highlighted the need for deposition techniques which allow for a high degree of control over film thickness and conformality. Many methods, such as chemical and physical vapor deposition, have made substantial progress towards meeting those requirements; however, molecular layer deposition (MLD) may be the ideal candidate for future development. MLD is an organic vapor deposition technique that takes advantage of sequential, self-limiting surface reactions, analogous to atomic layer deposition (ALD), whereby thin-film polymers can be deposited with angstrom-level thickness control even onto high aspect-ratio features. There are inherent constraints, however, to the variety of chemistries available for MLD, due to its vapor-phase nature, which precludes the use of solvents and many catalysts. As a result, most MLD polymers contain heteroatom-type connectivities and do not include new carbon-carbon bonding moieties, thus preventing the formation of many of the most common commercially available polymers.

Here, we discuss a new approach to MLD, photoactivated molecular layer deposition (pMLD), a process which provides new pathways to forming carbon-carbon bonds. In pMLD, monomers are activated upon exposure to UV light to create metastable radicals, which are then reacted with alkenes in a step-wise polymerization. Self-limiting bifunctional precursors are chosen which limit the extent of homopolymerization while enabling layer-by-layer growth. In this work, an alternating hydrocarbon-fluorocarbon polymer was deposited via pMLD using bifunctional diiodofluoroalkanes and dienes. It was determined using ellipsometry that the deposition has a constant growth rate and displays saturation behavior. X-ray photoelectron spectroscopy (XPS) analysis indicates the formation of new carbon-carbon bonds. By using alternate monomer backbones, we show that the composition follows a nearly 1:1 monomer deposition ratio, an indication that homopolymerization is minimized. In situ XPS annealing shows the fluoropolymer exhibits high temperature stability up to 400 ºC, similar to a pure polytetrafluoroethylene polymer. The films also display chemical resistivity to a variety of solvents, acids, and bases. Elemental mapping using Auger electron spectroscopy confirms that the fluoropolymer film can be patterned using a UV photomask. We also show that the pMLD film can be used for ALD inhibition, blocking up to 100 cycles of Pt ALD. The strategy described in this work enables a new scope of applications for MLD, whereby carbon-carbon bonds are formed, greatly expanding the MLD toolbox.

5:20pm **TF+SS-TuA10 Sputter-Deposited Porous Coatings for Solid Phase Microextraction***, **Tuhin Roychowdhury**, D.I. Patel, M.R. Linford,* Brigham Young University

Solid Phase Microextraction (SPME) is 'green method' for isolating target analytes from complex matrices. It works by placing a coated fiber near a sample such that the molecules of interest can be selectively extracted and concentrated. These captured species are then released into a chromatograph for separation, identification, and quantification. Popular, commercial SPME coatings suffer from various drawbacks that include solvent incompatibility, low capacity, limited lifetime, etc. These problems are addressed by our new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. Our approach includes sputtering silicon onto fiber substrates to produce columnar structures. These porous silicon nanostructures are further oxidized leading to a high density of silanol groups on their surfaces. We have now demonstrated that both silanes and ultrathin PDMS layers can be deposited on these surfaces. These coatings can be produced in various morphologies and thicknesses by manipulating the sputter and deposition conditions. For example, refractory materials like carbon can also sputtered onto these fibers to create porous morphologies, which should be beneficial for chromatography. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToFSIMS), and wetting . The performance of our 2 µm thick, porous, sputtered coatings has been compared to that of a thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for higher molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant due to their toxicity and carcinogenicity. These results are not the end of what is possible. Based on our work in this area we are convinced that further significant improvements in extraction efficiency and selectivity are possible.

5:40pm **TF+SS-TuA11 Interfacial Electron Transfer of Ferrocene Immobilized onto Indium Tin Oxide through Noncovalent Interactions***, **Caitlin Hanna**, J. Yang,* University of California, Irvine

Immobilization of molecular species onto electrode surfaces is a strategy for the modification of surface properties with molecular specificity. Attachment of molecular fuel forming catalysts to photovoltaic electrodes, for example, is a promising route to efficient solar fuel generation. Current attachment methods are synthetically difficult and can have adverse effects on the electrode performance. This report describes a non-covalent method for molecular immobilization onto indium tin oxide (ITO) surfaces. The fabrication, characterization, and electrochemical behavior of 1-pyrenylferrocene physisorbed onto ITO surfaces through π-π interactions is described. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry confirm the attachment of 1-pyrenylferrocene to the surface and highlight the stability of the system for aqueous electrochemical applications. The electron transfer kinetics between the ITO electrode and non-covalently attached ferrocene are compared to the kinetics of covalently-bound ferrocene. The kinetic studies of electron transfer show that electron transfer is ten times faster for non-covalently attached ferrocene than for covalently attached ferrocene.

6:00pm **TF+SS-TuA12 Vapor Phase Infiltration of Polymers with Intrinsic Microporosity: Structure and Chemical Separation Performance***, **Mark Losego**, E.K. McGuinness, F. Zhang, R. Lively,* Georgia Institute of Technology

Over 10% of the world's energy consumption goes to separating chemicals via thermal distillation. Membrane-based separation can drastically reduce these energy and financial costs, but membranes must be carefully designed to meet performance and durability needs. Polymers of intrinsic microporosity like PIM-1 are emerging membrane materials of interest for industrial separations. These materials can be readily formed into films and/or fiber bundles for rapid chemical separation. However, PIM-1 swells in many solvents (e.g., ethanol) and can suffer from long-term porosity collapse. We have been investigating the vapor phase infiltration of these PIM-1 materials with inorganic constituents to improve performance and long-term stability. These studies have revealed a number of surprising observations including that these materials can be loaded to an excess of 30 wt% inorganics using a single VPI exposure dose despite no indication of chemical binding between the organic and inorganic constituents. We currently believe this loading is due to an intermediate binding state between the metalorganic precursors and the PIM-1's nitrile group. This binding state is sufficiently stable to withstand 2 days of inert gas purging, yet when exposed to an oxidant and removed from the reaction chamber no permanent chemical reactions between inorganic and PIM-1 can be detected by XPS, NMR, or FTIR. After infiltration, these organic-inorganic hybrid membranes show unprecedented performance for a PIM, fully capable of separating small molecules in ethanol solvents that should swell and collapse the polymer's pores.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP
Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water*, **Pitambar Sapkota**, S. Ptasinska,* University of Notre Dame*; A. Cabrera,* Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors*, **Jordi Fraxedas**, K. Zhang, B. Sepulveda, M.J. Esplandiu,* Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain*; X. Garcia, J. Llorca,* Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain*; V. Perez-Dieste, C. Escudero,* Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study*, **Yufei Ni**,* University of California, Riverside*; F. Zaera,* University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its anime moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst*, **Sonal Singhal**, A.K. Shukla,* IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li^+ Transfer into Nanostructured TiO_2*, Tiffany Kaspar*, *T. Varga,* Pacific Northwest National Laboratory*; D.A. Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory*; A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

Surface Science Division
Room Hall B - Session SS-TuP
Surface Science Division Poster Session

SS-TuP1 Encapsulation of Metallic Nanoparticles near the Surface of Graphite*, Ann Lii-Rosales*[1,2]*,* *P.A. Thiel,* Iowa State University and Ames Laboratory

Graphite, in the bulk, is known to form graphite intercalation compounds (GICs) with certain elemental metals, for example, rare earths, alkali metals, and alkaline earths. These metals can insert between graphene sheets and alter the magnetic or transport properties of graphite. While intercalation in the bulk of graphite has received much attention, considerably less has been paid to intercalation near the *surface* of graphite, underneath only one (or a few) graphene layers. First of all, can one trap metals just beneath the graphite surface? Do the surface-intercalated metals adopt different structures compared to their bulk counterparts? What is the driving force for such surface intercalation? These questions motivate our work.

The presentation will encompass strategies for achieving *surface* intercalation of metals in graphite. In short, we find that trapping metal atoms just beneath the graphite surface requires two specific conditions: (1) ion-induced defects on the graphite surface, and (2) elevated temperature during metal deposition. We find that this strategy works for a variety of metals, and the growth temperature is metal-specific. Results on dysprosium, copper and ruthenium will be presented. We use scanning tunneling microscopy to probe and characterize the surface intercalation. Based on experimental results and density functional theory, we find that the intercalated metal atoms at the graphite surface adopt *much different* structures compared to those in bulk GICs – “encapsulated” may be a better descriptor than “intercalated”. Furthermore, metals that are not known to form bulk GICs *can* be encapsulated at the graphite surface. Finally, we find that some of the metals are well protected from atmospheric oxidation by the graphene overlayer. Our synthetic strategy opens up a new avenue for metals to interact with the graphite surface, and to create novel surface nano-structures.

SS-TuP2 Uncovering the Mechanism of Thermal Dry Etching of Cobalt Thin Films Using Hexafluoroacetylacetone (hfacH)*, Mahsa Konh,* *J. Zhao, A.V. Teplyakov,* University of Delaware

The initial steps of thermal dry etching of cobalt thin films with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) as the organic precursor were studied with in situ temperature-programmed desorption (TPD) and with X-ray photoelectron spectroscopy (XPS) supplemented with microscopic investigations. Comparison of the reaction of hfacH with oxidized and clean (sputtered) cobalt thin films suggested that partial surface oxidation is essential in designing dry etching schemes of this metal. On a clean surface, decomposition of the organic precursor molecule was the primary surface process. The oxidized cobalt surface can be reduced by a reaction with hfacH, releasing $Co(hfac)_2$ and water (as a side product). However, the thermal chemistry occurred at temperatures significantly higher than those required for industrial applications. The kinetic contribution to the overall etching process was investigated by exposing the oxidized cobalt films to hfacH at several temperatures and following the chemical and morphological changes of a surface. It was determined that exposure to hfacH affected the nanostructuring of the surface even at room temperature (making the surface rougher). Annealing this surface to 800 K produced a much smoother film following $Co(hfac)_2$ and water removal; however, at that point the films also started to produce microscopic level defects (pits). The optimization of surface temperature placed the upper limit of the process, before substantial surface decomposition of the hfacH precursor molecule and significant morphological changes took place, at 650 K. Further studies are required to explain the experimentally observed possibility of cobalt surface etching at temperatures as low as 440 K.

SS-TuP3 Revealing the Atomic Scale Insights for CO_2 Dissociation on the Rh(111) Surfaces at Ambient Pressure*, Won Hui Doh,* Institute for Basic Science (IBS), Republic of Korea*; J. Kim,* Institute for Basic Science (IBS), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS), Republic of Korea

Carbon dioxide (CO_2) in the atmosphere is one of the main cause of the greenhouse effect due to CO_2 molecules absorb the infrared radiation emitted by the Earth’s surface. Since the Industrial Revolution in 1750’s, the concentration of CO_2 in the atmosphere is continuously increased owing to increase of its emission in the economic sector such as electricity and heat production, industry, transport, and etc. Therefore, the utilization of CO_2 has received great attention from many researchers because of the challenging issue to use CO_2 as an energy resource.

A fully oxidized form of carbon e.g. CO_2, however, is a very stable compound which has two double bonds between carbon (C) and oxygen (O) in opposite direction. To facilitate the CO_2 utilization, as the first step of the reaction, the bond between C and O need to weaken or broken for further reactions. Rhodium is well known reducing material which can offer its electrons to the reactants. Previous research on CO_2 reduction reaction showing that CO_2 molecules have a bent structure or CO_3^{2-} after they adsorbed on a catalyst surface by using vibrational and spectroscopies such as IRARS and XPS. However, there is no direct observation for the bent structure of CO_2 on the catalyst surface. Here, we will show the first atomic-scale observation of bent CO_2 adsorption on Rh(111) surface as an intermediate by using near ambient pressure scanning tunneling microscope (NAP-STM). Furthermore, we will discuss the possible mechanism of CO_2 dissociation on Rh(111) based on the NAP-STM images of CO and O_2 adsorption structures on Rh(111) at NAP conditions.

SS-TuP4 Study of Spin Dependent Electrochemical Charge Transfer Across the Ferromagnetic Electrode/Solution Interface*, Mika Tamski,* *F. Blumenschein, C. Roussel, J.-P. Ansermet,* Ecole Polytechnique Fédérale de Lausanne, Switzerland

The Pauli Exclusion principle is known to result in spin dependent charge transfer, where the current is rectified for spins of the same orientation compared to the spins of opposite orientation.[1,2]

Similar spin selectivity has been observed for Ferromagnetic electrodes such as Nickel and Cobalt in electrochemical systems, where chiral molecules have been used as spin filters for selecting one spin orientation over the other. [3,4]

Here we report the progress concerning our studies of spin dependent charge transfer across a ferromagnetic-electrode/solution interface, using the following methodology (Fig.1, online at organiser's website):

1. Saturating the magnetization of the electrode and polarising the spins of radicals in the solution phase by applying a magnetic field $\boldsymbol{B_0}$.

2. Applying a negative potential to the electrode to induce a charge transfer from the electrode to the paramagnetic species in the solution.

3. Introducing spin-flips of the radical spins with resonant microwave irradiation $\boldsymbol{B_1}$.

4. Detecting the modulation of the reduction current as a function of modulation of the $\boldsymbol{B_0}$ or $\boldsymbol{B_1}$ amplitude, i.e. an electrically detected magnetic resonance (EDMR) experiment.

---

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

[2] **National Student Award Finalist**

References:

1 K. Ono, D. G. Austing, Y. Tokura and S. Tarucha, *Science*, 2002, **297**, 1313 LP-1317.

2 A. C. Johnson, J. R. Petta, C. M. Marcus, M. P. Hanson and A. C. Gossard, *Phys. Rev. B*, 2005, **72**, 165308.

3 P. C. Mondal, C. Fontanesi, D. H. Waldeck and R. Naaman, *Acc. Chem. Res.*, 2016, **49**, 2560

4 P. C. Mondal, P. Roy, D. Kim, E. E. Fullerton, H. Cohen and R. Naaman, *Nano Lett.*, 2016, **16**, 2806–2811.

SS-TuP5 Two-faced Steps: How Molecular Alignment does and does not Impacts O_2 Sticking Dynamics on Pt.

K. Cao, Leiden University, Nederland*; M. Kurahashi,* National Institute for Materials Science, Japan*; **Ludo Juurlink**,* Leiden University, Nederland

Adsorption and dissociation of O_2 on Pt are intensely studied reactions. In heterogeneous catalysis, it is claimed to be of high importance to automotive air pollution control. In electrochemistry, the oxygen reduction reaction limits the efficiency of hydrogen fuel cells. From previous dynamical and spectroscopic studies, it is well-established that O_2 does not dissociate as an elementary reaction on Pt(111). It requires trapping in a chemisorbed molecular state prior to dissociating. Surface corrugation enhances the sticking probability for O_2 at low incident energy, whereas at higher incident energy the influence depends on the step type causing corrugation. In this contribution, we study the origins of these findings combining two recently developed techniques. First, we apply a curved single crystal approach in combination with supersonic molecular beam techniques with high spatial resolution. At low incident energy, the enhanced reactivity is linear with step density and nearly identical for two different step types over a step density range covering approximately two orders of magnitude. At high incident energy, the enhancement mostly disappears. These result suggest energy-dependent dominance of parallel mechanisms causing sticking and dissociation. Second, we use spin-rotation state-selected and aligned O_2 to determined how rotation parallel and perpendicular to the (111) plane and the step direction affect dissociation on 'flat' Pt(533), Pt(553) and Pt(111) single crystals. At lower incident energy, activated molecular chemisorption on the (111) plane strongly favors helicoptering O_2 molecules. This effect diminishes with increasing kinetic energy. The A- and B-stepped surfaces show, on the contrary, at low incident energy no dependence on the orientation of the molecular axis upon impact. This is ascribed to the dominance of initial scattering into a physisorbed state preceding molecular chemisorption and dissociation. At higher incident energy, this mechanism loses its dominance and steps become stereodynamically selective. We observe a clear preference for O_2 molecules impacting with the molecular axis parallel to the step facet.

SS-TuP7 Crystallinity-Transport Investigations of Nanoscale Ru Conductors at Al_2O_3 and/or SiO_2 Interfaces

***Asim Khaniya**, S. Ezzat, W.E. Kaden, K.R. Coffey,* University of Central Florida

Enhanced scattering of charge-carriers at sufficiently small dimensions[1] (on the order of the mean free path of electrons), also known as the resistivity size-effect, leads to non-scalable increases in resistivity in conductors. As the trend of miniaturization continues in microelectronic fabrication, this size effect becomes a major challenge to current CMOS technology (Cu based) due to the loss of the majority of power at the interconnects due to their larger abundance. By using single-crystalline sub-nanometer metallic interconnects, room temperature ballistic conduction may be achieved. Within this general area of research, Ru has emerged as a promising candidate to replace Cu due to its weaker resistivity-thickness interdependence.[2] In practical applications, interconnects are necessarily in contact with isolating dielectric materials, and this work includes studies of Ru (0001) films epitaxially grown on c-axis sapphire, both with and without various silica capping layers in various states of crystallinity and chemical interaction with the underlying metal. The overall goal of the project is to measure the transport properties of the controllably different samples, while providing sufficient materials characterization to unequivocally establish correlations between changes in resistivity and changes in bulk/interface conductor properties.

To-date, efforts within our group have centered on physical characterization of films produced by collaborators from the Coffey Group in MSE at UCF, and early-stage efforts at reproduction of established SiO_2 thin-films via physical vapor deposition (PVD) within UHV. X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) have been used to demonstrate a high degree of both surface cleanliness and long-range crystal order following large-scale growth recipes carried out by the Coffey group. Further investigation has shown clear correlation between the extent of Ru oxidation and sheet resistivity following different annealing procedures during the film growth recipes. XPS, LEED, and low energy He^+ ion scattering spectroscopy (ISS) have been used to characterize our in situ SiO_2 film growth, which is highly dependent upon both coverage and oxidative crystallization temperature. Further, in-situ measurement of resistivity of Ru(0001) and SiO_2/Ru(0001) films will be made and additional atomically localized information will be collected using scanning tunneling microscopy (STM).

SS-TuP8 Iron Oxide Surface Transformations Revealed by AP-XPS for Ammonia Synthesis

***Mikhail Trought**,* Michigan Technological University*; E.J. Crumlin, S. Nemsak,* Advanced Light Source, Lawrence Berkeley National Laboratory*; K.A. Perrine,* Michigan Technological University

The industrial synthesis of ammonia, known as the Haber-Bosch process[1, 2], occurs at high temperatures and pressures where hydrogen (H_2) and nitrogen (N_2) react to produce ammonia (NH_3). The dissociation of nitrogen is known as the rate-limiting step on the surface of an iron oxide catalyst.[3-6] At equilibrium conditions, this reaction is well-known, however the surface transformations of the iron oxide single crystal surfaces have not been explored in the near-ambient pressure (intermediate) regime, which may allow for a better understanding of the role of the surface sites and transformations under pressure regimes between traditional surface science (in ultra-high vacuum) and reaction conditions (high pressures).

Synchrotron radiation ambient pressure-X-ray photoelectron spectroscopy (AP-XPS) was used to measure changes in the surface structure and oxidation states of single crystal Fe_3O_4(001) (magnetite) and α-Fe_2O_3(0001) (hematite) surfaces near-ambient pressure conditions. Adsorption of N_2, H_2, and O_2 on single crystal Fe_3O_4(001) and α-Fe_2O_3(0001) surfaces was measured as a function of temperature and pressure to gain a better understanding of the fundamental surface reactions associated with ammonia formation. In particular, the shape and states in the valence band photoemission spectra were examined to measure the affect of oxidation and reduction of the surfaces.[7] The valence band region helped to identify the states associated with the Fe^{2+} and Fe^{3+} cations in each compound highlighting the differences in structure between magnetite, hematite and the transformations that occurred due to the oxidative and reductive environments. The states present in the N1s, Fe2p and O1s regions complemented the changes in the valence band region observed on the iron oxide surfaces. The results reveal N_2 adsorbs on Fe_3O_4(001) but not α-Fe_2O_3(0001). These studies give insight into the complexity of adsorption processes and surface transformations during heterogeneous catalysis that merge surface science experiments with reaction conditions.

1. G. Ertl, *Zeitschrift Fur Anorganische Und Allgemeine Chemie*, 2012, **638**, 487-489.
2. G. Ertl, M. Grunze and M. Weiss, *Journal of Vacuum Science & Technology*, 1976, **13**, 314-317.
3. G. Ertl, *Angewandte Chemie-International Edition*, 2008, **47**, 3524-3535.
4. T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens and R. Schlogl, *Angewandte Chemie-International Edition*, 2013, **52**, 12723-12726.
5. G. A. Somorjai and N. Materer, *Topics in Catalysis*, 1994, **1**, 215-231.
6. D. R. Strongin and G. A. Somorjai, *Journal of Catalysis*, 1989, **118**, 99-110.
7. R. J. Lad and V. E. Henrich, *Physical Review B*, 1989, **39**, 13478.

SS-TuP9 Surface Energies of Thin Oxides of Si(100) as Function of Thickness, Composition and Surface Processing

***Saaketh Narayan**, J.M. Day, N. Herbots, A. Brimhall, A. Mascareno,* Arizona State University*; A. Krishnan,* Harvard University*; S.D. Whaley,* Arizona State University*; R.B. Bennett-Kennett,* Stanford University*; K.L. Kavanagh,* Simon Fraser University, Canada

Processing modifies hydroaffinity, reactivity, and total surface energy, γ^T, of semiconductor oxides. Si(100) and its oxides are studied, including native oxides, conventional thermal SiO_2, Rapid Thermal Oxides (RTO), Rapid Thermal Annealed (RTA) oxides, RCA processed Si, Herbots-Atluri (HA) passivated [1] Si, alpha-quartz SiO_2, and oxides after HF-based etching. Correlating surface energies of Si(100) and SiO_2 to composition and processing can reproducibly establish the metrology needed for wafer bonding. Cross-bonding is key in bonding conducted at T < 220°C, or NanoBonding™, [2,3] for Si(100) to SiO_2, GaAs(100), and $LiTaO_3$. Si(100) and Si(111) samples investigated include B-doped p- and p+ wafers, and P-doped n- and n+ wafers.

The surface energy of 50 wafers is measured via Three Liquid Contact Angle Analysis (3LCAA) using the van Oss-Chaudhury-Good (vOCG) model for semiconductors and insulators. The γ^T includes Lifshitz-van der Waals interaction, γ^{LW}, interaction with electron donors, γ^+, and with acceptors, γ^-. Reproducibility of contact angle measurements to extract γ^T, γ^{LW}, γ^+, and γ^- is achieved by metering µL droplets of 18 MΩ deionized H_2O, glycerin, and α-bromonaphthalene in a class 100/ISO 4 laminar flow hood. 4 contact angles are extracted from each droplet and its reflection through 18 MP images analyzed automatically via the Drop and Reflection Operative Program (DROP) which removes subjectivity and speeds up analysis. 30 droplets yield 120 angles, with an accuracy of 3%.

MeV Ion Beam Analysis (IBA) combining <111> channeling with nuclear resonance yields ^{16}O coverage, which is then correlated to γ^T, γ^{LW}, γ^+, and γ^-. Native oxides on p- Si are always hydrophilic, with a γ^T of 53 ± 2 mJ/m^2. RCA wafers have a lower γ^T of 47.3 ± 0.5 mJ/m^2, as RCA removes impurities, but are still relatively hydrophilic. Next, RTA oxides exhibit a lower γ^T than RCA oxides, as thicker oxides are more hydrophobic, corroborated by higher ^{16}O coverage. H-A wafers have a lower ^{16}O coverage but also a more hydrophobic γ^T of 37.3 ± 1 mJ/m^2, being terminated with ordered $Si_2O_4H_4$. RTO on H-A wafers yields the most hydrophobic surfaces with γ^T = 34.5 ± 0.5 mJ/m^2. IBA on native oxides of p- Si detects 13.3 ± 0.3 ^{16}O ML, while IBA on H-A and HF etched Si detects 11.8 ± 0.4 ^{16}O ML. IBA on RTA and RTO oxides show that thicker oxides yield more hydrophobic surfaces. In summary, 3LCAA in conjunction with IBA yields new insights in the relationship between γ^T, oxygen coverage, and processing.

---

[1] Herbots N. *et al*, US Pat N° 6613677 (2003), 7,851,365 (2010).

[2] Herbots, N. *et al*, US Pat. N° 9,018,077 (2015) 9,589,801 (2017)

[3] Herbots N., Islam R., US Pat. Pend. (2018)

SS-TuP10 Space Weathering Effects at the Surface of Thin-Film Aluminosilicate Model Regolith

***Bijoya Dhar**, W.E. Kaden,* University of Central Florida

Space weathering effects on volatile-rich airless bodies have been studied far less extensively, than those anhydrous interfaces. Although the presence of volatile resources has been established by recent space exploration missions, the fundamental physics and chemistry behind volatile formation and sequestration, associated with radiation processing of regolith, is yet to be thoroughly explored. Therefore a systematic and integrated study of the effect of radiation processes on regolith is needed to better understand the fundamental driving forces governing the volatile transformation at the interface of such bodies. Accordingly, the overall goal of the project is an in situ study of regolith, irradiated with laboratory-based sources within a UHV system, mimicking solar wind processes on airless bodies in space.

To carry out this work, our group is leveraging established thin-film recipes to generate and characterize a well-ordered regolith simulant within our multi-purpose UHV system. Herein we use aluminosilicate ($Al_xSi_yO_z$) sheets as model regolith. The $Al_xSi_yO_z$ film will be grown on a ruthenium (Ru) substrate via sequential PVD of Al and Si in the presence on O_2. The Ru is cleaned with repeated Ar^+-sputtering/annealing. XPS and He^+ ISS have been used for cleaned Ru to ensure surface cleanliness (no detectable contaminants) and LEED for long-range crystal order (sharp 1x1 hexagonal pattern). Initial silica (SiO_2) thin-film growth has been employed to establish both coverage and oxidative crystallization temperature. Using the calibrated Si flux and relative XPS sensitivity factors, Al flux will be calibrated, and both will be used to create bilayer $Al_xSi_yO_z$ film. In addition to the XPS, ISS and LEED, atomic scale confirmation of planar/crystalline silicate layers will be provided by STM analysis.

To simulate solar wind processing of model regolith, we will use irradiation facilities available in our lab, such as an electron gun, an ion gun, and an X-ray source. The physical and chemical characterization of radiation-induced defects to the fabricated $Al_xSi_yO_z$ sheet (like those previously reported by others for SiO_2 film) will be investigated with the in-house equipment. Previously established experiments used to investigate SiO_2 will be helpful to study the electron-stimulated desorption of volatiles. In addition, $Al_xSi_yO_z$ film transference to other supports will be attempted in support of collaborative efforts with others.

Our methods encompass surface science methodologies for radiation investigation on regolith samples, which will help to minimize the gaps in knowledge related to space weathering effects on the airless bodies.

SS-TuP11 Identification of Surface Processes in Individual Minerals of a Complex Ore through the Analysis of Polished Sections using Polarization Microscopy and X-ray Photoelectron Spectroscopy (XPS)

***Dhamelyz Silva Quiñones**,* UTEC, Perú*; C.H. He,* University of Delaware*; J.C. Rodriguez,* UTEC, Perú*; A.V. Teplyakov,* University of Delaware*; C. Benndorf,* UTEC, Perú

The changes at the surface level of a mineral during ore processing is of fundamental importance for the improvement of strategies aimed at increasing the efficiency of metal extraction. This task is often difficult due to the refractory behavior of minerals and the deficiency of valuable metals within them. Specifically, surface processes such as metal readsorption (preg-robbing) on specific minerals are difficult to evaluate, this process can block or encapsulate the valuable mineral and affect negatively the extraction process. In this study, we show a powerful approach, through which surface processes in individual minerals are identified by combining polarization microscopy (MP) and X-ray photoelectron spectroscopy (XPS). A silver-containing polymetallic sulfide ore from the Peruvian central Andes (pyrite-based with small amounts of galena and covellite) is evaluated, and we track the gradual changes in the sample during the course of leaching with cyanide. The polarization microscopy technique identifies mineralogical species such as pyrite, galena, and covellite, while XPS provides evidence of readsorption of lead on the surfaces of pyrite and covellite after leaching, possibly as lead oxide or thiosulfate. The surface of pyrite does not show significant changes after leaching process according to the microscopic result, although species of oxidized iron are detected together with the readsorption of lead by XPS. The methodology shown here is a tool of significant importance for understanding complex surface processes affecting various minerals during metal extraction and highlights the importance of using surface analytical techniques for the development of novel strategies in the mining industry.

SS-TuP12 Effect of Surface Roughness, Etch Pits, and Adsorbates on the Surface Phonon Density of States of Graphite

***Krishnan Swaminathan-Gopalan**, K. Stephani,* University of Illinois at Urbana-Champaign

Gas-surface interactions are encountered in a wide variety of disciplines and a detailed understanding of the underlying physics is critical. When a gas-phase particle strikes a surface, it can undergo adsorption, direct impact reactions, or inelastic scattering. These processes are coupled with the phonon bath at the material interface. During the interaction, energy transfer occurs both between and within the sub-systems (substrate and gas particle). A number of mechanisms including multi-phonon processes, translational and internal mode excitations may be captured by the evaluation of the detailed scattering kernels and transition matrix of the gas-phonon interaction. Such a framework provides a powerful alternative to full molecular dynamics (MD) for computing various surface interaction quantities such as accommodation coefficients, adsorption and reaction probabilities, etc. Further, since this framework captures the underlying microscopic details, and can be extended to describe the system in the state of extreme non-equilibrium. These theoretical models have been shown to provide excellent agreement with experiments.

In this work, we will focus on understanding the effect of (i) random surface roughness, (ii) etch pits, and (iii) adsorbates on the phonon density of states of carbon using Molecular dynamics (MD). The phonons at the surface are qualitatively and quantitatively different from the bulk due to the broken symmetry. In addition, the roughness of engineering material surfaces affects the phonon distributions. Furthermore, the gas-surface interactions also alter the PDOS due to the presence of adsorbates on the surface and removal of surface atoms due to surface participation reactions. This results in a highly coupled and dynamic system. Random surface roughness in MD will be obtained via irradiation with low energy particles. The effect of varying height and density of the defective region on the PDOS of this system will be investigated. The etch pits produced as a result of removal of surface atoms resembles a semi-ellipsoid with larger diameters and shorter depth. Here, the phonon distribution will be characterized as a function of both diameter and depth of the etch pits. Finally, the effect of adsorbates on the PDOS will be studied in terms of bond strength (physisorbed vs chemisorbed) and surface coverage.

SS-TuP13 Variation of Structure Colors of Copper with LIPSS(Laser-Induced Periodic Surface Structure) by Femtosecond Laser Irradiation*, **TaeHoon Park**, J.H. Kim, T.Y. Hwang, J.J. Kang,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; K.B. Kim,* Sejong University, Republic of Korea*; H.S. Lee,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

The Laser-Induced Periodic Surface Structure (LIPSS) formed under femtosecond laser irradiation has been a way to change optical, tactile, hydrophobic properties, etc. without chemical reaction. Specially, the LIPSS can be applied to enhance the visual perception of skin materials in order to meet the user's aesthetic choice of mobiles, auto vehicles, electronics, etc. It has been reported through many studies that the structure color by LIPPS is due to the refraction of the light by periodically nano-scaled structure, however, its variation of structure colors has not been studied generally on the microstructures such as pitch and depth of nano-scaled microstructure. In this study, the metal substrates consisting of pure copper were processed with the condition of femtosecond laser irradiation with the scan rate from 4 mm/s to 20 mm/s and the scan space of 40 µm. The color difference (ΔE) of periodically nano-scaled structure obtained by femtosecond laser irradiation was measured by a multi angle spectrophotometer and quantified by the value of L*a*b* chromaticity diagram. The periodically nano-scaled structures of pure copper showed the roughness (R_a) from 29 nm to 50 nm at the pitch of approximately 280 nm. The brightness was decreased as 15% with an increase of roughness due to a diffused refraction from the surface. The value of L* was ranging from 4 to 81, a* was from 4 to 19 and also b* was from 2 to 24 in the chromaticity diagram of pure copper as detected with tilt angles of 15° to 110°. The calculated ΔE from these results were widely shown from 1.5 to 77, which means that distinctive colors can be realized although the composition of material is not different. It could be expected that the structure color was sufficiently controlled by the periodically nano-scaled structures from femtosecond laser process, and was to be applied at various skin materials.

SS-TuP15 Oxidation of Nb(100) and Kinetics of Surface to Bulk Transport and Extension to Nb_3Sn*, **Rachael Farber**, D.R. Veit, S.J. Sibener,* The University of Chicago

Niobium (Nb) is commonly used in superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance (R_s) and high cavity quality factor (Q) at ~ 2 K. Nb cavities are, however, highly susceptible to localized surface heating, resulting in quenching of the superconducting properties. To minimize quenching, much work has been done to understand factors influencing SRF cavity performance for the clean and oxidized Nb surface. In this work, we have investigated the structural evolution of oxidized Nb(100) under ultra-high vacuum (UHV) conditions to elucidate the structural evolution of the (3×1)-O ladder structure following exposure to O_2. Auger electron spectroscopy (AES) was used to determine oxygen coverage and surface structure was determined using scanning tunneling microscopy (STM). The (3×1)-O Nb(100) surface was exposed to O_2 at 300 K and annealed to various substrate temperatures to facilitate oxygen dissolution. Dissolution kinetics elucidated the surface to bulk oxygen transport mechanism. STM showed the decomposition of the ordered (3×1)-O ladder structure during oxygen dissolution, indicating the importance of oxygen concentration on surface structure. As the fundamental limits of Nb SRF cavities are being realized, it is crucial that alternative SRF materials be studied. Nb_3Sn has been identified as a most promising next generation SRF material with higher Q as well as the ability to operate at much higher temperatures, greatly reducing cryogenic infrastructure costs. Ongoing work is focusing on developing preparation methods leading to more homogeneous Nb_3Sn films. *In situ* Sn doping on (3×1)-O Nb(100) combined with surface sensitive techniques such as AES, XPS, and LT-STM will hopefully allow for the diffusion mechanism for Sn on Nb to elucidated, leading to improved procedures for Sn infusion and materials growth.

Extending Additive Manufacturing to the Atomic Scale Focus Topic

Room 102B - Session AM+NS+SS-WeM

Nanofabrication with Focused Electron Beams (8:00-10:00 am)/Atomic Scale Manipulation with Focused Electron Beams (11:00 am-12:20 pm)

Moderator: Ondrej Dyckoe, Oak Ridge National Laboratory

8:00am **AM+NS+SS-WeM1 3D Nano-Printing via Focused Electron Beams: An Emerging Technology for Novel Applications***, **Harald Plank**, R. Winkler, J. Sattelkow,* Graz University of Technology, Austria*; J.D. Fowlkes,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville **INVITED**

3D-printing of functional structures has emerged as an important technology in research and development. While being reliable on the micro and sub-micron scale, the extension to the nanoscale is still a challenging task. Among the very few direct-write techniques on that scale, focused electron beam induced deposition (FEBID) is one of the promising candidates as this technology allows fabrication of functional nano-structures on almost any material and substrate morphology in a single-step process. Based on strong fundamental progress in recent years, FEBID was demonstrated to be capable of fabricating complex, freestanding 3D nano-architectures with individual branch diameters down to 20 nm. Together with the increasing availability of precursors with different functionalities, FEBID is advancing from a versatile research tool into a predictable and reliable 3D nano-printer, which opens up new opportunities for advanced applications.

In this contribution, we start with the basic principles of 3-dimensional printing via FEBID, complemented by simulations for deeper insight into the fundamental processes that are operative. In the following, we present a variety of 3BID based proof-of-principle studies to demonstrate the capabilities of this direct-write technology. This ranges from scientifically oriented applications, such as plasmonics, magnetics and nano-mechanics toward industrially relevant concepts for scanning probe microscopy related tip fabrication, such as electrical, thermal and optical 3D nano-probes. Finally, we overview some of the remaining challenges and provide an outlook on future activities.

8:40am **AM+NS+SS-WeM3 3D Nanoprinting using an Electron Beam: Simulations and Computer-aided Design***, **Jason Fowlkes**,* Oak Ridge National Laboratory*; R. Winkler,* Graz Centre for Electron Microscopy, Austria*; B.B. Lewis,* Carl Zeiss Microscopy, LLC*; A. Fernandez-Pacheco, L. Skoric, D. Sanz-Hernandez,* University of Cambridge*; M.G. Stanford, E. Mutunga, P.D. Rack,* University of Tennessee*; H. Plank,* Graz University of Technology, Austria **INVITED**

The deposition of complex 3D nanoscale objects with prescribed geometry and function constitutes a major goal of nanoscience. Additive assembly is the ideal approach to efficiently deposit 3D materials. Focused electron beam induced deposition (FEBID) is a resist-free, direct–write method suitable for the additive deposition of materials on both planar and nonplanar surfaces. During FEBID, a focused electron beam is scanned along the substrate surface inducing the deposition and condensation of absorbed precursor molecules, often an organometallic, delivered locally by an in-situ gas injector. Until recently, 3D deposition using FEBID was mostly a trial-and-error exercise lacking a reliable framework to deposit a wide range of geometries.

A design environment specific to beam induced deposition will be presented that has enabled the deposition of complex, 3D nanoscale mesh style objects spanning nanometer to micrometer length scales. A complementary 3D simulation of FEBID provides a predictive capability that aides in the design of more complex 3D deposits. The purpose of this design/simulation capability is to generate the primary electron beam coordinates and beam exposure dwell times necessary for the experimental deposition of 3D mesh objects, with a reduced fill factor, i.e., geometries required for the design of metamaterials, high–aspect ratio sensors/actuators and/or nanomagnetic/optical lattices.

The simulation reveals that precursor surface diffusion and electron beam induced heating, in particular, can impose unwanted mesh object distortions if not properly accounted for. This general rule applies for several precursors under picoampere, millisecond beam exposure using typical local precursor fluxes consistent with high vacuum scanning electron microscope operation. Compensation for these influences can be applied in either the CAD phase, as geometric distortions, or through the introduction of exposure pulsing which acts to mitigate the development of transient mass/heat gradients. The role of simulation in design will also be explained in the context of the proximity effect due to scattered electrons, specifically their role in inducing unwanted deposition. Simulation results are limited to cases where complementary experiments converge with simulated predictions in terms of the final deposit geometry and the electrical current collected dynamically during deposition.

11:00am **AM+NS+SS-WeM10 Single Atom Scale Manipulation of Matter by Scanning Transmission Electron Microscopy***, **Stephen Jesse**, O. Dyckoe, S.V. Kalinin,* Oak Ridge National Laboratory **INVITED**

Fabrication of atomic scale structures remains the ultimate goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates to seminal experiments by Don Eigler, who demonstrated single atom manipulation. However, stability and throughput remain issues. The molecular machines approach harnesses the power synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss research activity towards a third paradigm — the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on atomic scales. Traditionally, STEM's are perceived only as imaging tools and beam induced modifications as undesirable beam damage. Our team and several groups worldwide have demonstrated that beam induced modifications can be more precise. We have demonstrated ordering of oxygen vacancies, single defect formation in 2D materials, and beam induced migration of single interstitials in diamond like lattices. What is remarkable is that these changes often involve one atom or small group of atoms, and can be monitored real-time with atomic resolution. This fulfills two out of three requirements for atomic fabrication. I will introduce several examples of beam-induced fabrication on the atomic level, and demonstrate how beam control, rapid image analytics, better insight through modelling, and image- and ptychography based feedback allows for controlling matter on atomic level.

This research is supported by and performed at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

11:40am **AM+NS+SS-WeM12 Single Atom Modification of 2D Materials: Fabrication and Electronic Structure***, **Demie Kepaptsoglou**, F. Hage,* SuperSTEM Laboratory, UK*; T. Susi, J. Kotakoski, J. Meyer,* University of Vienna, Austria*; Y.C. Lin, K. Suenaga,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Hardcastle,* University of Leeds, UK*; U. Bangert,* University of Limerick, Republic of Ireland*; JA. Amani, H. Hofsaess,* University of Göttingen, Germany*; Q. Ramasse,* SuperSTEM Laboratory, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

The past decade has seen incredible progress in the ability to isolate and manipulate two-dimensional crystals. Due to their unique structure and dimensionality, it is possible to confine charge carriers in two dimensions, resulting in peculiar physical, chemical and electronic properties. Such novel properties can be further controlled and tuned through defects such as single atom dopants, interfaces, etc. This defect engineering takes place quite literally at the atomic level, where a combination of low voltage scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and *ab-initio* calculations provides not only the most powerful means of characterization, but also a unique tool for manipulating the single atom structures and engineer their electronic interaction with the host matrix. This approach was recently used to demonstrate that low energy ion implantation (of dopants such as N and B) can be successfully implemented to introduce single substitutional defects with excellent retention rates and without affecting the structural integrity of the surrounding graphene matrix. Atomically-resolved EELS experimental data reveals the bonding signature of the dopants themselves and their impact on the surrounding lattice. *Ab initio* calculations, in excellent agreement with the experiment, confirm the nature of the excited states being probed by the EELS experiments and the electronic structure reconfiguration of the doped material around the single atom dopants. Results directly confirm the possibility of tailoring the plasmonic properties of graphene in the ultraviolet waveband at the atomic scale, a crucial step in the quest for utilizing it's properties toward the development of plasmonic and optoelectronic devices. The gentle STEM observation conditions can also be used to controllably drive the diffusion of substitutional dopants through single layer graphene, one atomic jump at a time. Atomically precise manipulation with STEM relies on recent advances in instrumentation that have improved the instruments' stability and their beam positioning abilities. While momentum transfer from highly energetic electrons often leads to atom ejection, interesting dynamics can be induced when the transferable kinetic energies are comparable to bond strengths in the material. For instance, a combined experimental and theoretical study revealed that for Si dopants manipulated in the STEM by 60keV electrons these jumps are not due to impacts on the Si atom, but to sub-threshold impact events on the surrounding C atoms. This approach suggests that STEM could emerge as an alternative method for the direct assembly of nanostructures.

Electronic Materials and Photonics Division

Room 101A - Session EM+AN+MI+SS-WeM

Surface and Interface Challenges in Electronics and Photonics

Moderators: Andy Antonelli, Nanometrics, Michael Filler, Georgia Institute of Technology

8:00am **EM+AN+MI+SS-WeM1 Few Monolayer Atomic Layer Deposition (ALD) to Engineer New Surfaces and Interfaces*, Parag Banerjee,*** Washington University in St. Louis **INVITED**

Atomically precise modification of surfaces and interfaces with few monolayer material leads to improved understanding and significant enhancements in properties, performance and reliability of heterogeneous materials and devices. This talk highlights the impact of few monolayer insulators, wide bandgap semiconductors and metals, deposited using atomic layer deposition (ALD) on a variety of surfaces and interfaces with direct relevance to electronic and photonic devices.

The first part of this talk deep dives into the process science of ALD in its early cycles. The nature and structure of few monolayer ALD films is highlighted. In particular, configurational state and entropy of adlayers during every half-cycle of ALD[1] is exploited to exquisitely manipulate nucleation and growth of metallic Ru thin films.[2]

In the second part of this talk, applied aspects of few monolayer engineering of surfaces and interfaces is discussed. Case studies included are the non-linear optical phenomena on Au-Al_2O_3 and Au-ZnO surfaces,[3] high performance photocatalysts for CO_2 photoreduction,[4] improved optoelectronic responses from surface passivated CuO nanowires[5] and few monolayer Ta_2O_5 to improve reliability of electrochromic windows.[6]

Regardless of the application, ALD at its ultimate thickness limit holds true potential for surface and interface engineering. The control of this process appears to be remarkably simple and yet, has hidden complexities that continue to push the boundaries of discovery of new materials and concept devices.

Relevant references:

[1] Zhengning Gao, Fei Wu, Yoon Myung, Ruixiang Fei, Ravindra Kanjolia, Li Yang, and Parag Banerjee, J. Vac. Sci. Technol. A **34** (1), 01A143 (2016); Lei Shi, Zhengning Gao, Zhaonan Liu, Yoon Myung, and Parag Banerjee, Chem. Mater. **29** (13), 5458 (2017).

[2] Zhengning Gao, Duy Le, Ravindra Kanjolia, Charles Dezelah, Jacob Woodruff, Talat Rahman, and Parag Banerjee, Under review (2018).

[3] Zhengning Gao, Mallik M.R. Hussain, Domenico de Ceglia, Maria A. Vincenti, Andrew Sarangan, Imad Agha, Michael Scalora, Joseph A. Haus, and Parag Banerjee, Appl. Phys. Lett. **111**, 161601 (2017).

[4] W-N. Wang, F. Wu, Y. Myung, D.M. Niedzwiedzki, H.S. Im, J. Park, Parag* Banerjee, and Pratim* Biswas, * co-corresponding authors, ACS Appl. Mater. Interfaces **7** (10), 5685 (2015).

[5] Sriya Banerjee, Zhengning Gao, Fei Wu, Yoon Myung, and Parag Banerjee, Under Review (2018).

[6] Yang Wang, Jongwook Kim, Zhengning Gao, Omid Zandi, Sungyeon Heo, Parag Banerjee, and Delia Milliron, Chem. Mater. **28**, 7198 (2016).

8:40am **EM+AN+MI+SS-WeM3 Lattice-alignment mechanism of SiGe on Sapphire*, HyunJung Kim,*** National Institute of Aerospace*; S. Choi,* NASA Langley Research Center

In the conventional heteroepitaxy processes, the deposition of dissimilar materials has been made with the same or similar crystal structure and perfect or nearly matching lattice constants, such as Ge/Si (diamond cubic), InAs/GaAs (zinc-blende), and GaN/Al_2O_3 (hexagonal/trigonal). On the other hand, the super-heteroepitaxy of two semiconductors with dissimilar crystal structures such as SiGe (diamond cubic)/Al_2O_3 (trigonal) is not readily achievable but requires scrupulous manipulation of growth conditions for single crystal formation. Epitaxial growth patterns of SiGe on *r*-plane and *c*-plane of sapphire substrates show 90°-rotated and 60°-rotated twin defects, respectively [1,2].

A team at NASA Langley Research Center developed a technique for super-hetero-epitaxy of single crystal SiGe growth; diamond-cubic structure of SiGe on trigonal structure of the *c*-plane sapphire substrate by a transformed lattice structure under a new lattice-alignment model [2]. Although the growth conditions were effective for the formation of single crystal film, how the mechanism or physics of single crystal formation of SiGe at the interface of sapphire was not theoretically and experimentally defined with the order of atomic scale level in arrangement. This work presents the interfacial image of SiGe/Al_2O_3 using high-resolution transmission electron microscope (HRTEM) to show the SiGe/Al_2O_3 interfacial bonding for superheteroepitaxy mechanism. The first two atomic layers of the SiGe are Si-rich where Si atoms match with the surface oxygen lattice of the Al_2O_3 substrate. After the Ge composition increases, the monolayer spacing is also increased due largely to the dominance of Ge composition since the lattice constant of Ge is bigger than that of Si. These results highlight the importance of a cleanliness of sapphire substrate, the Si-affinity to oxygen that ties up Si- of SiGe with the oxygen of sapphire, and eventually causing the deformation of SiGe cubic structure for super-heteroepitaxy [3]. From the essential understanding of the SiGe/Al_2O_3 interface mechanism, both low temperature SiGe super-heteroepitaxy and the III-V or II-VI semiconductor epitaxy are possible.

References:

[1] W.B. Dubbelday, K.L. Kavanagh, J. Cryst. Growth, 222 (2001), pp. 20-28.

[2] Y. Park, G.C. King, S.H. Choi, J. Cryst. Growth, 310 (2008), pp. 2724-2731.

[3] H. J. Kim, D. Adam, S. H. Choi, Acta Materialia, 145 (2018), pp. 1-7.

9:00am **EM+AN+MI+SS-WeM4 An Effort to Resolve Band Offset Anomalies in ZnO/GaN Heterostructures*, Monu Mishra*[1]*,*** *A. Gundimeda, V. Vandana, G. Gupta,* CSIR-National Physical Laboratory, India

Gallium Nitride (GaN) and Zinc Oxide (ZnO) are well established wide band gap (WBG) semiconductors facilitating potential application in futuristic energy-efficient opto/micro-electronics technology. Despite of owing the merits of both semiconductors, the understanding of ZnO/GaN heterostructures is still posing challenges. The available reports display anomalies amongst calculated valence band offset (VBO) and defect state of ZnO/GaN interface. The influence of surface and interfacial properties perturbs the electronic structure, localized charge density and defect states at the interface, yet the impact of these properties on VBO requires more scientific attention. Hence, sharp interfaces of ZnO/GaN heterostructures (ZnO thickness = 2, 5 and 8 nm) were fabricated via atomic layer deposition (ALD) of ZnO on MOCVD grown highly crystalline GaN epilayer and further investigated by HR-XPS, UPS and PL spectroscopy. The impact of ZnO thickness on band bending (upwards & downwards), surface/interface dipole strength and defects states (vacancies, interstitials, donor/acceptors etc.) on valence & conduction band offsets (VBO/CBO) were thoroughly analysed. It was observed that the VBO at the interface was reduced via 0.6 eV as the ZnO thickness was increased from 2 nm to 8 nm which was ascribed to interface dipole strength along with dramatic change in localized BB (downwards-flatband-upwards). A type-II band alignment was perceived at all ZnO/GaN interfaces though the nature & contribution of defects states (especially oxygen vacancies and zinc interstitials) varied incommensurately. The defect band spectra revealed a blue shift (~502 eV) which correspond to the conversion of yellow-green emission in ultrathin ZnO/GaN heterostructure (2 nm ZnO) to characteristic green emission in bulk ZnO. The analysis revealed that the thickness of ZnO overlayer in ZnO/GaN heterostructure significantly alters the electronic structure and defect states at the interface and thus the resolution of anomalies in the present analysis would be useful for the fabrication of ZnO/GaN heterostructure based efficient optoelectronic devices.

9:20am **EM+AN+MI+SS-WeM5 Stress Relaxation in the Si-SiO2 System and its Influence on the Interface Properties*, Daniel Kropman,*** *T. Laas,* Tallinn University, Estonia*; A. Medvids,* Riga Technical University, Latvia

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and

---

[1] **National Student Award Finalist**

lattice mismatch appear in the Si-SiO$_2$ system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO$_2$ system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO$_2$ system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si$_3$N$_4$ deposition on SiO$_2$. Different sign of the thermal expansion coefficient of the SiO$_2$ and Si$_3$N$_4$ on Si allow to modifay the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100^{0}C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies),while at a oxidation temperature 1200^{0}C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensil IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO$_2$ (E' centers).At an intermediate oxidation temperature tensil stresses in Si and compressive stresses in SiO$_2$ may bee equal and compensate each others. It has been find that at oxidation temperature 1130^{0}C IMS at the Si-SiO$_2$. interface are lower than at 1100^{0}C and 1200^{0}C. Lower defect dencity on samples crossection microphotos obtained by SEM and PD dencity diminishing.in samples oxidized at 1130^{0}C confirmed thise suggestion.In Fig,2 the EPR signal and IR absorbtion line-width dependence on the oxidation time is shown. It can bee seen ,that EPR signal and IR absorbtion line-width at 1100 cm^{-1} dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate .In slowly cooled samples the increase of the EPR signal is accompanied by the decrease of Δν but,in fast cooled samples EPR signal and Δν increase simultaneously with increase oxidation time.

Absent of the cooling rate influence on the PD density and Δν dependence on the oxidation time at I(t) and Δν(t) dependence intersection points show, that IMS by an appropriate choice of the SiO$_2$ film thickness dissapear.

9:40am **EM+AN+MI+SS-WeM6 Unique Sensitivity to Deep Trap States Demonstrated by CREM of Broad Bandgap Dielectric Layers***, **Hagai Cohen,*** Weizmann Institute of Science, Israel*; K.X. Steirer,* Colorado School of Mines

Chemically resolved electrical measurements (CREM) present an efficient and sensitive means for studies of structural-electrical inter-relationships in heterostructures. Operated in-situ to x-ray photoelectron spectroscopy (XPS), the technique is yet far from being fully exploited. Recent progress in our CREM instrumentation has, however, opened new opportunities to which this report is dedicated. Using broad-bandgap dielectric layers, such as SiO$_2$, SiON and ZnOS, we tested the CREM resolving power and sensitivity to charge trap states. These experiments yielded band diagrams with fine details on charge traps, which typically require the application of advanced optical techniques combined with the electrical characterization tools.

In addition, an intriguing process of doubly triggered conductance in ZnOS was observed. The ZnOS layers exhibited very poor conductance under either electrical or optical input signals, whereas simultaneous application of the two yielded extremely high sample currents. Based on the in-situ derived band diagram, a comprehensive explanation of the effect is provided. Moreover, we show how the CREM analytical tool can also provide a potential activator of future related devices.

11:00am **EM+AN+MI+SS-WeM10 Fabrication of Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides: ALD vs CVD***, **Riya Bose**, A.D. Dangerfield,* University of Texas at Dallas*; S.M. Rupich,* University of Texas*; Y.J. Chabal, A.V. Malko,* University of Texas at Dallas

Semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their size/shape/composition tunable properties and inexpensive solution based synthesis techniques. Integration into solid state devices requires deposition of NQD films, and often a controlled assembly of multilayered NQD structures to ensure maximum light absorption and optimum efficiency of the devices. However, thin film fabrication is found to degrade its properties compared to NQDs in solution, especially a decrease in the photoluminescence (PL) quantum yield (QY) is frequently observed. Also, the bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer until each NQD layer is rendered insoluble by means of any surface passivation technique. Surface passivation techniques also play a critical role to protect the deposited layers from oxidation and deterioration. An attractive method to passivate NQD films during the deposition as well as from environmental exposure is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of NQD films, they mostly attend to charge transfer-based devices and aim to improve carrier moblities. Typically, such studies report a significant quenching of the PL intensity after encapsulation. In this study, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of NQD films and how it, along with the ALD parameters, affects their PL properties. With the aid of in-situ FTIR and ex-situ XPS measurements during Al$_2$O$_3$ deposition on oleic acid capped CdSe-ZnS core-shell nanocrystals, it is observed that the interaction of the metal precursor trimethyl aluminium (TMA) with the surface of the NQDs leads to the reorganization of the ligands as well as replaces Zn, leading to PL intensity quenching. In order to prevent this, we opted for a pulsed chemical vapour deposition (CVD) like approach for metal oxide deposition where simultaneous purging of both the metal and oxygen precursors leads to formation of metal oxide in a gas phase in the immediate vicinity of the NQD surface. We found that minimization of TMA interaction with the NQDs' surface indeed leads to enhancement of the PL intensity and elongation of carrier PL lifetime. These measurements provide clear indication of defect-free surface passivation proving that CVD-like Al$_2$O$_3$ encapsulation is a suitable technique for controlled deposition of multilayered NQD structures that preserves its optoelectronic properties.

11:20am **EM+AN+MI+SS-WeM11 The Role of Surface Oxides for the Optoelectronic Performance of III-V Semiconductor Nanowires***, J. Colvin, A. Troian, O. Persson, A. Mikkelsen, **Rainer Timm,*** Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. We have previously studied surfaces and surface oxides of semiconductor NWs by scanning tunneling microscopy and spectroscopy (STM/S) [3] as well as X-ray photoemission spectroscopy [4]. Here, we will correlate the surface properties of InAs and InP NW heterostructures with their electrical and photovoltaic behavior, which has been measured for individual upright-standing NWs using the STM tip as local nanoprobe [5].

InP and GaInP pin-junction NWs have been cleaned from their native oxide by annealing under atomic hydrogen background and re-oxidized by exposure to ambient conditions. By illuminating the InP NWs that were contacted by the STM nanoprobe, we observed a decrease of the open-circuit voltage from 0.75 V to 0.70 V upon native oxide removal and an increase back to 0.76 V upon re-oxidation, confirming the need of surface passivation for improving InP solar cells. However, the ideality factor of the NW pin-diodes remained constant at n = 1.82 upon oxide removal, but improved to n = 1.67 upon re-oxidation. Furthermore, our XPS results indicate the outdiffusion of Zn dopants from the p-doped NW segments, forming a Zn-rich shell around the NW.

A more significant effect of the presence of native surface oxide was found for InAs NWs which consist of one segment of wurtzite and one segment of zincblende crystal structure. Upon removal of the native surface oxide, we obtained an increase in conductivity of these NWs by two orders of magnitude, while reference NWs with pure wurtzite structure showed a slight decrease in conductivity with the same surface treatment. This effect can be explained by a staggered type-II surface band alignment at the wurtzite/zincblende interface of oxidized NWs, which turned into flat-band conditions upon oxide removal, as confirmed by nano-focus XPS measurements.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

[3] M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

[4] R. Timm *et al.,* Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.,* Nano Lett. **15**, 4865 (2015).

[5] R. Timm *et al.,* Nano Lett. **13**, 5182 (2013).

11:40am **EM+AN+MI+SS-WeM12 Photonic Annealing of 2D Transition Metal Dichalcogenides for Tailored Optical Properties***, **Rachel Rai**, K. Gliebe,* University of Dayton; Air Force Research Laboratory*; N.R. Glavin, R. Kim, A. Jawaid, R. Wheeler, L. Bissell,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Thin layers of transition metal dichalcogenides (TMD) have attracted significant interest in the field of optoelectronics due to their unique light absorption and emission properties in the visible frequency range. Development of bright, flexible, large area emission sources based on 2D materials using photonic annealing represents an exciting opportunity for future quantum systems. Here we introduce new correlations relating the optical properties of WSe_2, a well-known single photon emitter, to post-processing annealing techniques to include lasers, broadband radiation, and nanoscale electron beams. Modulation of the total energy flux during growth of amorphous TMD material to develop purely amorphous materials or materials with nanoscale nuclei was employed by the authors to examine effects of pre-existing nuclei on crystallization kinetics (i.e., activation energy) and the resulting optical properties. We correlate the wavelength and intensity of photoluminescence from WSe_2 deposited on plasma treated and as-received flexible substrates and present techniques to control film continuity and the areal density of free edges from islands on discontinuous films for tuning the intensity of optical emission. A significant increase in photoluminescence intensity is accompanied by a change in domain boundary density, correlating well to theory. Furthermore, examination of quantum confinement effects by producing nanoscale crystalline areas (between 5-50 nm) with precisely controlled volumes via electron beam radiation provides insight on light emission mechanisms.

12:00pm **EM+AN+MI+SS-WeM13 Polarity Control of GaN Nanowires on Diamond: Experiment and Theory***, **Karin Larsson**,* Uppsala University, Sweden*; M. Hetzl, M. Kraut, T. Hoffmann, M. Stutzmann,* Technical University Munich, Germany

III-nitride nanowires on diamond substrates are of current interest for two different potential applications: (i) selectively grown n-type AlGaN nanowires on p/i – diamond are promising for the electrical control and the efficient optical and electrical readout of individual NV-centers in diamond as qubits and (ii) AlGaN/diamond n/p-heterodiodes are an interesting option for future ultraviolet LEDs and laser diodes. For both applications, the polarity of AlGaN nanowires grown on diamond has a strong influence on the optoelectronic properties of the heterojunctions, because the polarization-induced interface charge strongly influences the details of the diamond/III-nitride band alignment. Thus, the growth of nanowire arrays with randomly fluctuating polarity will have a negative influence on the electronic properties of the heterojunctions.

In this presentation, we will discuss recent experimental results concerning the control of GaN nanowire polarity on diamond (111) substrates via different surface termination treatments (hydrogenation, oxygen termination, nitrogen radical exposure [1]). Systematic experimental investigations have shown that even very well ordered periodic nanowire arrays deposited by Selective Area Growth exhibit a high degree of polarity disorder. Diamond is a well-suited substrate for these investigations, since it supports several different types of stable surface structures which only differ by about one monolayer and have a strong influence on the preferred nanowire polarity. The effect of different surface terminations on nanowire polarity will be recapitulated. Furthermore, we complement these experimental investigations by theoretically studying the effect of diamond surface termination on the energetically preferred GaN polarity. First principle DFT-calculations are used to calculate the interface energies and the corresponding atomic configurations of the different diamond/GaN interfaces. Strong variations observed in the interface chemistry between diamond and GaN nanowires will be discussed based on the available experimental and simulation data.

[1] M. Hetzl et al., Nano Lett. 17, 3582 (2017)

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeM

Mechanisms and Reaction Pathways of Heterogeneously Catalyzed Reactions

Moderator: Johan Gustafson, Lund University

8:00am **HC+SS-WeM1 Surface Reactions of Methanol on Fe_3O_4(001) and Pd/Fe_3O_4(001) Model Catalysts***, **Matthew Marcinkowski**, N. Doudin, R.S. Smith, B.D. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory

Single atom catalysts offer potential improvements in reactivity, selectivity, and decreased catalyst cost, but are often difficult to characterize and stabilize. Iron oxides are frequently used as catalyst supports, and recent studies have shown that Fe_3O_4(001) magnetite can stabilize isolated atoms of many transition metals.[1] This property makes the (001) surface of magnetite ideal for model studies of the catalytic activity of supported single atoms. In this study, we examine the adsorption and reaction of methanol on Fe_3O_4(001) and Pd/Fe_3O_4(001) surfaces using a combination of scanning tunneling microscopy, temperature programmed desorption, and x-ray photoelectron spectroscopy. We find that a monolayer of methanol saturates on Fe_3O_4(001) at a coverage of 5.8×10^{14} molecules/cm^2, which corresponds to one methanol per every surface Fe^{3+} ion. The majority of methanol desorbs molecularly by 280 K. Above 300 K, methanol dissociates to form methoxy and hydroxyl species.[2] The maximum coverage of methoxy that can be achieved is 1.2×10^{14} molecules/cm^2. The methoxy species form an ordered layer adsorbed on the Fe^{3+} sites above the subsurface cation vacancies. At elevated temperatures, the methoxy species react via one of two processes: recombining with hydroxyl to desorb as additional molecular methanol at 350 K, or further dehydrogenation to produce formaldehyde above 500 K. Production of formaldehyde is limited to 2.3×10^{13} molecules/cm^2. On single Pd atoms on Fe_3O_4(001), the production of formaldehyde above 500 K is suppressed while a new formaldehyde channel is observed at 300 K. Increasing the Pd atom concentration increases the magnitude of the low-temperature channel. Interestingly, the total amount of formaldehyde produced in these two channels remains constant throughout the range of Pd concentrations studied, indicating that the methoxy species are formed on the Fe_3O_4 substrate and Pd atoms only facilitate the conversion of methoxy species to formaldehyde. However, the appearance of the lower temperature reaction channel for formaldehyde shows that the Pd atoms lower the reaction barrier to dehydrogenate methoxy to formaldehyde by almost a factor of two.

1. R. Bliem et al. *Phys. Rev B***92,** 075440 (2015)
2. O. Gamba et al. *Top. Catal.***60,** 420 (2017)

8:20am **HC+SS-WeM2 Hydrogen Activation and Spillover on Single Palladium Atoms Supported on Fe_3O_4(001) Surface***, **Nassar Doudin**,* Pacific Northwest National Laboratory*; J. Cheng Liu,* Tsinghua University, China*; M.D. Marcinkowski, M.-T. Nguyen,* Pacific Northwest National Laboratory*; J. Li,* Tsinghua University, China*; V.-A. Glezakou,* Pacific Northwest National Laboratory*; G.S. Parkinson,* Vienna University of Technology, Austria*; R. Rousseau, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysts have recently attracted great attention due to their ultimate metal efficiency and the promise of novel properties. However, at the atomic level, little is known about their stability, interactions with the support, and mechanisms by which they operate. Recently it has been shown that on Fe_3O_4(001) surface, single metal atoms can be stabilized to temperatures as high as 700 K [1]. This high stability makes Fe_3O_4(001) a promising support for model studies of single atom catalysts. Here, we present a room-temperature study of H_2 dissociation on single Pd atoms on Fe_3O_4(001) followed by H atom spillover via scanning tunneling microscopy (STM) and density functional theory (DFT). The exposure to H_2 at 300 K results in the appearance of bright double protrusions located on surface iron (Fe_S) sites. Such protrusions were observed previously [2] following the adsorption of atomic H and hydroxyl formation (O_SH) on bare Fe_3O_4(001). By analogy, we attribute the features observed here to O_SH species. The DFT calculations further reveal that H_2 dissociates heterolytically and spills over both hydrogen atoms onto Fe_3O_4(001). When the exposure to H_2 is increased, the density of O_SH's is also observed to increase. With approximately every fourth surface oxygen atom hydroxylated, many areas show a local order with O_SH's spaced according to the $(\sqrt{2}\times\sqrt{2})R45°$ surface reconstruction. STM data further indicate that H atoms diffusion is accelerated in the presence of coadsorbed water. At highest coverages of O_SH's (approximately every second oxygen atom hydroxylated), the reconstruction is lifted, and the Pd atoms become destabilized . These studies clearly demonstrate that single Pd atoms can efficiently dissociate H_2 that spills over onto a reducible oxide support that can be extensively hydroxylated.

[1] R. Bliem et al. Science 346, 6214 (2014).

[2] G. S. Parkinson et al. Phys. Rev. B 82, 125413 (2010).

8:40am **HC+SS-WeM3 Model Studies on Ligand-assisted Heterogeneous Catalysis***, **Swetlana Schauermann,*** Christian-Albrechts-University Kiel, Germany **INVITED**

Identifying the surface processes governing the selectivity in hydrogenation of α,β-unsaturated carbonyl compounds on late transition metals is crucial for the rational design of new catalytic materials with the desired selectivity towards C=O vs. C=C bond hydrogenation. In the present talk it will be shown that the selectivity of these reactions can crucially depend on the presence of specific ligand-like surface co-adsorbates. Specifically, I will present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) surface and Pd nanoparticles supported on a model oxide support.[1] We show for the first time that selective hydrogenation of the C=O bond in acrolein to form the desired reaction product – an unsaturated alcohol propenol – is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface highly selective towards propenol formation. By applying pulsed multi-molecular beam experiments and *in operando* IRAS we identified the chemical nature of the spectator and the reactive surface intermediate as oxopropyl and propenoxy species, respectively. The evolution of the surface concentration of the propenoxy intermediate monitored spectroscopically was found to closely follow the propenol formation rate detected in the gas phase.

In the second part, the catalytic surfaces modified with chiral adsorbates will be discussed. In heterogeneous catalysis, such chiral modification of the non-chiral metal surfaces allows to turn the catalytic processes asymmetric and produce enantiopure compounds. We will discuss the atomistic details of the chiral modification as well as the interaction between the chiral modifiers and the prochiral adsorbates on well-defined Pt(111) surface.

References:

1. Dostert, K.-H.et al, *J. Amer. Chem. Soc.* **2015**, *137*, 13496-13502.

9:20am **HC+SS-WeM5 *In situ* Structural Studies and Gas Phase Visualization of Model Catalysts at Work***, **Sara Blomberg**[1], J. Zetterberg, J. Zhou, J. Gustafson, E. Lundgren,* Lund University, Sweden

Catalysis is widely used in the production process of chemicals, pharmaceuticals, fuels or ammonia synthesis. The catalyst accelerates the chemical reaction but without being consumed. The materials system of a catalyst is complex and as a result, the catalytic process in most cases is not fully understood, and fundamental studies of the catalyst at operating conditions are close to impossible.

In the last decades, a number of *in situ* experimental techniques have been developed operating at semi-realistic condition to extend the fundamental knowledge on catalytic reactions and to bridge the pressure gap. We have therefore used Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) for surface and gas-phase studies and Planar Laser-induced Fluorescence (PLIF) for gas phase visualization.

Using APXPS to investigate the CO oxidation over a Pd(100) single crystal[2], we observe a pressure dependent CO desorption temperature, and therefore a pressure dependent ignition temperature of the reaction. The experiments were carried out by slowly increasing the temperature of the Pd(100) in a 1:1 ratio of CO and O_2 and systematically increasing the total pressure. The increasing ignition temperature of the catalyst is observed in conjunction with an increasing oxygen coverage on the surface measured immediately after the ignition. Remarkably, no CO could be detected neither in the gas phase nor adsorbed on the surface after the ignition of the reaction, despite a highly active surface.

To investigate the gas phase in more detail, we have developed PLIF, where an image of the gas distribution close to the surface is obtained [2]. PLIF was used to study *in situ* the change of the gas phase during CO oxidation, where the images visualize the build-up of a boundary layer of CO_2 close to the active surface, and the reaction is mass transfer limited by the diffusion of CO. Within this boundary layer the gas composition is significantly different as compare to the composition detected at the outlet of the reactor by a mass spectrometer (MS)[3]. The drastic drop in the CO pressure close to the surface explain the lack of detected CO in the APXPS experiments, which result in a partial pressure of CO below the detection limit of the APXPS.

[1] S. Blomberg et al. In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap, Phys Rev Lett, **110** (2013) 117601.

[2] Sara Blomberg *et alJ. Phys.: Condens. Matter***28** (2016) 453002

[3] J. Zetterberg et al. Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence. , Nat Commun, **6** (2015) 7076.

9:40am **HC+SS-WeM6 Adsorption, Thermal Stability, and Kinetics of Atomic Oxygen at Ag(111) and Ag(110) Surfaces***, **Sara Isbill**[2], S. Roy,* University of Tennessee Knoxville

Transition-metal surfaces are commonly used to catalyze transformations of small organic compounds, but the catalyst structures and catalytic mechanisms are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate adsorption, thermal stability, and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces and examine their effects on the structural and catalytic properties of silver. On Ag(111), it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption. In contrast, on Ag(110), surface adsorption remained more favorable than subsurface adsorption at all studied coverages. Our thermodynamic and kinetic models of O/Ag(111) based on DFT-computed equilibrium constants and activation energies show that the stability of subsurface oxygen is sensitive to coverage, thereby indicating that the participation of subsurface oxygen in catalysis would strongly depend on coverage. Overall, our results provide valuable qualitative insight into the formation and motion of subsurface oxygen on Ag(111) and Ag(110) surfaces, the importance of metal-adsorbate charge transfer in these systems, and the possible roles of subsurface oxygen in catalytic oxidation by silver.

11:00am **HC+SS-WeM10 Understanding the Intrinsic Surface Reactivity of Multilayer vs. Single-layer PdO(101) on Pd(100)***, **Jason Weaver**, V. Mehar,* University of Florida*; M. Kim,* Ohio State University*; M. Shipilin,* Lund University, Sweden*; M. van den Bossche,* Chalmers University of Technology, Gothenburg, Sweden*; J. Gustafson,* Lund University, Sweden*; L. Merte,* Chalmers University of Technology, Gothenburg, Sweden*; U. Hejral,* Lund University, Sweden*; H. Gronbeck,* Chalmers University of Technology, Gothenburg, Sweden*; E. Lundgren,* Lund University, Sweden*; A. Asthagiri,* Ohio State University

Understanding the intrinsic reactivity of different types of O-rich phases that form on Pd surfaces is central to developing accurate models of oxidation catalysis. In this talk, I will discuss results of a recent study in which we used temperature programmed reaction spectroscopy (TPRS) and surface IR spectroscopy (RAIRS) as well as DFT calculations to investigate the intrinsic CO oxidation activity of single and multiple-layer PdO(101) structures grown on Pd(100) in UHV. We find that CO binds more strongly on multiple vs. single-layer PdO(101) (~110 vs. 40 kJ/mol), and that CO oxidizes negligibly on single-layer PdO(101) whereas nearly 90% of a saturated layer of CO oxidizes on multiple layer PdO(101) during TPRS experiments. RAIRS further shows that CO molecules adsorb on both bridge and atop-Pd_{cus} sites (coordinatively-unsaturated Pd sites) of single-layer PdO(101)/Pd(100), while CO binds exclusively on atop-Pd_{cus} sites of multilayer PdO(101). Our DFT calculations reproduce the much stronger binding of CO on multiple layer PdO(101) as well as the observed binding site preferences, and reveal that the stronger binding is entirely responsible for the higher CO oxidation activity of multiple vs. single layer PdO(101)/Pd(100). We show that the underlying O-atom bonding partners, present only in multiple layer PdO(101), modify the electronic states of the Pd_{cus} atoms in a way that enhances the CO-Pd_{cus} bonding. Lastly, we show

---

[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[2] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

that a simple kinetic model, with energetics determined from the present study, predicts that the intrinsic CO oxidation rates achieved on both single and multilayer PdO(101)/Pd(100) can be expected to exceed the gaseous CO diffusion rate to the surface during steady-state CO oxidation at elevated pressures, even though the intrinsic reaction rates are 4-5 orders of magnitude higher on multiple vs. single layer PdO(101)/Pd(100). Our findings help to resolve seemingly disparate conclusions about the CO oxidation activity of the single and multiple layer PdO(101) structures, as determined from previous *in situ* vs. UHV measurements, and highlight the importance of characterizing the intrinsic reactivity of catalyst surfaces for developing first-principles kinetic models that can accurately reproduce surface reactivity over a wide range of conditions.

11:20am **HC+SS-WeM11 Simultaneous Study of Catalyst Structure, Gas Phase and Morphology***, **Sebastian Pfaff**, J. Zhou, S. Albertin,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; J. Gustafson, S. Blomberg, E. Lundgren, J. Zetterberg,* Lund University, Sweden

CO oxidation has long been studied as a model reaction for catalysis diagnosis. In recent time, increased focus has been given to study well-defined single crystal surfaces to further investigate the details of the involved reaction mechanisms[1]. During the past years, new techniques have been developed to study both the surface structure and gas phase in a semi-realistic environment such as High Energy Surface X-Ray Diffraction (HESXRD)[2] and Planer Laser Induced Fluorescence (PLIF)[3]. HESXRD is a technique well suited to gain knowledge about the surface structure, but without any macroscopic spatial resolution. Planar Laser Induced Fluorescence (PLIF) is a technique which excels at determining the structure and composition of the gas phase. One of the main advantages of this technique is its high spatial and immediate temporal resolution. Additionally, LED surface reflectance techniques have been developed, which provide a simple way of producing a macroscopic map of the entire single crystal, clearly visualizing changes on the surface[4].

In this work, the mentioned techniques were combined at the beamline P07 at PETRA III while performing CO oxidation over a Pd(100) single crystal sample. We have shown a clear spatial correlation between a reduced surface reflectance and an increased CO2 concentration in the gas phase. Additionally, through the sub-second temporal resolution of PLIF, we have determined the delay between a measurable change of the surface structure using HESXRD and a change in gas composition as the catalyst switches between high and low activity.

References

1. Freund, H.-J., et al., *CO Oxidation as a Prototypical Reaction for Heterogeneous Processes.* Angewandte Chemie International Edition, 2011. **50**(43): p. 10064-10094.

2. Gustafson, J., et al., *High-Energy Surface X-ray Diffraction for Fast Surface Structure Determination.* Science, 2014. **343**(6172): p. 758-761.

3. Zetterberg, J., et al., *Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence.* Nature Communications, 2015. **6**: p. 7076.

4. Zhou, J., et al., *Simultaneous Imaging of Gas Phase over and Surface Reflectance of a Pd(100) Single Crystal during CO Oxidation.* The Journal of Physical Chemistry C, 2017. **121**(42): p. 23511-23519.

11:40am **HC+SS-WeM12 New Catalysis for Light Alkanes – From Methane Functionalization to Light Akenes***, **Johannes Lercher**,* Pacific Northwest National Laboratory and TU München, United States of America/Germany **INVITED**

The abundant availability of light alkanes opened new opportunities to synthesize light alkenes and oxygenates, challenged only by the high dispersion of the carbon sources, requiring dedicated processes. Three different principal catalysis pathways will be discussed, the conversion of methane to methanol, the oxidative dehydrogenation of ethane and the dehydrogenation of propane to propene, eventually followed by aromatization. For the three approaches it will be shown, how the atomistic understanding of the catalyst properties including an atomistic description of the active site by combining electron microscopy and X-ray absorption spectroscopy and the molecular pathways by identifying elementary steps via NMR spectroscopy and isotope labeling allows to drastically develop catalysts and catalytic pathways. Combining rigorous kinetics with spectroscopy allowed for all three cases to describe rates linked to specific active sites and maximize their concentration. The potential and limitations of this fundamental approaches to discover new catalysts and improve existing will be discussed.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces***, **Ethan J. Crumlin**,* Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS***, **Rachel Komorek**, X.F. Yu, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

Key words: in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

References

1. Y Wang, G Zhu, E Wang, Electrochemical behavior of FAD at a gold electrode studied by electrochemical quartz crystal microbalance. *Anal. Chem. Acta.* (1997), **338**, 97-101.

2. W Chen, J-J Chen, R Lu, C Qian, W-W Li, H-Q Yu, Redox reaction characteristics of riboflavin: A fluorescence spectroelectrochemical analysis and density functional theory calculation. *Bioelectrochemistry* (2014), **98**, 103-8.

3. B Liu, et al., In situ chemical probing of the electrode–electrolyte interface by ToF-SIMS. *Lab Chip* (2014), **14**, 855-9.

4. J Yu et al., Capturing the transient species at the electrode-electrolyte interface by *in situ* dynamic molecular imaging. *Chem. Comm*. (2016), **73**, 10929-11206.

9:00am **PC+AS+BI+EM+PB+SS-WeM4 Electrowetting of Liquid Drops Revisited by XPS***, **Sefik Suzer**, P. Gokturk, B. Ulgut,* Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10^{-2} – 10^{5} Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

*This work is partially supported by TUBITAK through Grant No. 215Z534

9:20am **PC+AS+BI+EM+PB+SS-WeM5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques***, M. Chi, **Wenpei Gao**,* Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

Acknowledgements: Research supported by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:00am **PC+AS+BI+EM+PB+SS-WeM10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology***, **Didier Arl**, T. Da Cunha, N. Adjeroud, K. Menguelti, M. Gerard, D. Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

Surface Science Division
Room 203C - Session SS+HC-WeM
Catalytic Alloys: Understanding Heterogeneity

Moderators: April Jewell, Jet Propulsion Laboratory, Jean-Sabin McEwen, Washington State University

8:00am **SS+HC-WeM1 Toward Surface Science-informed Design of Bifunctional Deoxygenation Catalysts***, **J. Will Medlin**,* University of Colorado Boulder **INVITED**

A major challenge for catalysis is controlling the selectivity for desired reactions of biomass-derived compounds, including selective removal of oxygen atoms. Surface-level studies have the potential to provide deep insights into catalytic reaction mechanisms for deoxygenation. Using single-crystal metal surfaces as model catalysts, the elementary steps associated with both selective and non-selective reaction pathways can be mapped out in significant detail. Surface science studies have also elucidated roles of the different metals within bimetallic catalysts for complex deoxygenation reactions. This presentation will focus on how insights from such model studies have been used to inform efforts to design catalysts for deoxygenation and other key reactions of biomass-derived compounds. It will also discuss complications arising from the so-called pressure and materials "gaps" associated with the use of model surfaces, as well as opportunities for addressing these apparent limitations.

8:40am **SS+HC-WeM3 Computationally Assisted Correlative STEM and EXAFS Characterization for Multiscale Structure Determination of Tunable Rh/Au Bimetallic Nanoparticle Catalysts***, S. House, C.S. Bonifacio,* University of Pittsburgh*; J. Timoshenko,* Stony Brook University*; P. Kunal, H. Wan, Z. Duan, H. Li,* University of Texas at Austin*; **Judith Yang**,* University of Pittsburgh*; A.I. Frenkel,* Stony Brook University*; S. Humphrey, R. Crooks, G. Henkelman,* University of Texas at Austin

The acceleration of rational catalyst design by computational simulations is only practical if the theoretical structures identified can be synthesized and experimentally verified. Bimetallic catalysts have the potential to exceed the selectivity and efficiency of a single-component system but adding a second metal greatly increases the complexity of the system. Additionally, variation in the elements' mixing patterns and reconfiguration can affect the reaction mechanisms and thus catalytic performance [1]. Most experimental tools for the characterization of nanoparticles (NPs) provide structural data at the relevant length scales, but not enough to unambiguously determine the structure. Here we present our correlative theory-experiment design approach for addressing this issue, through application to the complex structures of Rh/Au bimetallic hydrogenation catalysts. Our calculations predict this system to exhibit superior allyl alcohol hydrogenation performance compared to single-element catalysts due to the ability to tune the hydrogen binding on the surface [2]. In this study, Rh/Au bimetallic NPs of different metal mixing ratios were synthesized via microwave heating and characterized using synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy and scanning transmission electron microscopy (STEM). EXAFS samples particle ensembles to extract information about atomic bonding (coordination, bond distances, etc.). TEM provides direct local characterization, down to the atomic scale, of particle size, morphology, and elemental distribution. The conventional approach to interpreting EXAFS – fitting to bulk reference spectra – is problematic for bimetallic NPs. We overcome this by using the STEM data to inform the generation of metal NP structures, calculated using interatomic potentials under the frame work the modified embedded-atom method (MEAM). EXAFS spectra for these structures were simulated and compared against the experimental EXAFS to iteratively refine the models, producing more atomic structures that were consistent with all experimental data, and will be more accurate for subsequent theoretical calculations. This work demonstrates that correlating the local characterization of TEM with the many-particle information from EXAFS grants a multiscale understanding not achievable with either approach alone.

[1] R. Ferrando, J. Jellinek, R.L. Johnston, Chem. Rev. **108** (2008), p. 845-910.

[2] S. Garcia, *et al.*, ACS Nano **8** (2014), p. 11512-11521.

9:00am **SS+HC-WeM4 Designing Heterogeneous Alloy Catalysts from First Principles and Surface Science***, **Charles Sykes,*** Tufts University

In this talk I will discuss a new class of metallic alloy catalysts called *Single Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.[1-5] These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between the atomic scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. Over the last five years the concepts derived from our surface science and theoretical calculations have been used to design *Single Atom Alloy* nanoparticle catalysts that can perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective chemical reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis and Michaelides at UCL that predicts reactivity trends of 16 different *Single Atom Alloy* combinations for important reaction steps like activation of H-H, C-H, N-H, O-H and C=O bonds. This project illustrates that the field of surface science is now at the point where it plays a critical role in the design of new heterogeneous catalysts.

References:

[1] Kyriakou et al. Science **335**, 1209 (2012).

[2] Marcinkowski et al. Nature Materials **12**, 523 (2013).

[3] Lucci et al. Nature Communications **6**, 8550 (2015).

[4] Liu et al. JACS **138**, 6396 (2016).

[5] Marcinkowski et al. Nature Chemistry **10**, 325 (2018).

9:20am **SS+HC-WeM5 Extracting Diffusing Parameters for Cu and S from Surface Segregation Data Recorded with AES on a Ni-Cu(S) Ternary Alloy***, **Jacobus Terblans,*** University of the Free State, South Africa*; X.-L. Yan,* University of the Free State, China*; J.Y. Wand,* Shantou University, China*; H.C. Swart,* University of the Free State, Republic of South Africa

The catalytic selectivity and activity of Cu-Ni bimetallic catalysts, used for oil hydrogenation, have been investigated extensively over the years. A catalytic surface that is Cu rich have higher selectivity than a Ni rich surface. The Cu-Ni alloy system has a simple phase diagram and forms a solid solution in the entire compositional range. In this study the segregation of Cu and S to the surface of a Cu-Ni alloy with 21.3 at.% Cu and 7 ppm S was measured by using Auger electron spectroscopy (AES) coupled with a linear programmed heater. It was found that first the Cu segregated to the surface and reached a maximum surface coverage of 40 %. Once the Cu reached a maximum surface coverage, it started to desegregate as it was replaced by the S that was also segregating to the surface. The measured segregation data were fitted by Fick's and Guttmann's ternary segregation models and the diffusing parameters (namely segregation energy (ΔG), interaction parameter (Ω), pre-exponential factor (D_0) and the diffusion activation energy (Q)) for both Cu and S were extracted from the data.

9:40am **SS+HC-WeM6 Atomic and Electronic Structure of CoO Nanoislands on Au(111)***, **Ana Sanchez-Grande,*** IMDEA Nanoscience, Spain*; J. Rodriguez-Fernandez,* Aarhus University, Denmark*; E. Carrasco, B. Cirera, K. Lauwaet,* IMDEA Nanoscience, Spain*; J. Fester,* Aarhus University, Denmark*; R. Miranda,* Universidad Autonoma Madrid, Spain*; J.V. Lauritsen,* Aarhus University, Denmark*; D. Ecija,* IMDEA Nanoscience, Spain

Oxides have found applications in various problems in the fields of chemistry, physics and materials science, notably for use in catalysis, encouraging investigation of fundamental properties of oxides. Hereby, transition metal oxides have been proposed as promising catalysts in the oxygen evolution reaction for water splitting, of crucial relevance in clean energy. Equipped with state-of-the-art scanning probe and sample-average techniques, atomistic insights for FeO [1] and CoO [2], [3] and their activity towards water splitting have been recently reported.

Despite this activity, there is a lack of knowledge about the precise atomic and electronic structure of most of these oxides. To understand better the activity of such catalysts, we have selected CoO nanoislands as an archetype model catalyst for water splitting. Our results show the complex atomic and electronic structure of CoO islands on Au(111), revealing the emergence of a Moiré pattern within the nanoislands. Such nanostructures show a higher density of states in the conduction band at the top moirons inside the nanoislands, while present an increase of the valence band states at the borders of the islands and at the bottom moirons inside the nanoislands. Importantly, oxygen dislocation lines induce profound electronic changes in adjacent regions (beta regions) within the nanoislands.

The exposure of such catalyst to water highlights that activity towards water splitting depends on substrate temperature. At room temperature [3], the water is adsorbed and dissociated, affording the formation of hydroxyls, which are located predominantly at the bottom moirons. However, at low temperatures the water is adsorbed intact exclusively on the beta regions and can be manipulated with the STM tip, affording a multi-level electronic molecular nano-switch.

Our results shed light into the atomistic adsorption and dissociation of water on a very promising catalysts and reveal that such a process is temperature dependent.

References:

[1]: Parkinson, G. S., Novotný, Z., Jacobson, P., Schmid, M. and Diebold, U. J. Am. Chem. Soc., **133** (32), 12650-12655 (2011).

[2]: Fester, J., García-Melchor, M., Walton, A. S., Bajdich, M., Li, Z., Lammich, L. and Lauritsen, J. V. Nat commun, **8**, 14169 (2017).

[3]: Walton, A. S., Fester, J., Bajdich, M., Arman, M. A., Osiecki, J., Knudsen, J. and Lauritsen, J. V. Acs Nano, **9** (3), 2445-2453 (2015).

11:00am **SS+HC-WeM10 Using Water as a Co-catalyst in Heterogeneous Catalysis to Improve Activity and Selectivity***, **Lars Grabow,*** University of Houston **INVITED**

"What happens when you add water?" is possibly the most frequently asked question after presentations in heterogeneous catalysis. In this talk, I will demonstrate that this question is indeed paramount and that the presence of even minute amounts of water can drastically change reaction rates and product selectivities. Examples include water-mediated proton hopping across a metal-oxide surface, oxidation of carbon monoxide at the gold/titania interface, and hydrodeoxygenation of phenolic compounds over titania supported ruthenium catalysts. Together, these examples demonstrate that water can act as co-catalyst in a variety of catalytic reactions and by varying the amount of water it may be possible to tune reaction rates and product selectivity.

11:40am **SS+HC-WeM12 Experimental and Theoretical Evaluation of Water Chemistry on Two-dimensional Silica and Aluminosilicate***, **Jin-Hao Jhang,** G.S. Hutchings,* Yale University*; J.A. Boscoboinik,* Center for Functional Nanomaterials Brookhaven National Laboratory*; E.I. Altman,* Yale University

The participation of water in zeolites is widely seen in catalysis, ion-exchange, and wastewater treatment. Water adsorption, dissociation and desorption all play critical roles in forming catalytically active Brønsted and Lewis acid sites. Recently, two-dimensional (2D) silica and aluminosilicate bilayers were fabricated on different substrates successfully. Prior studies have suggested that protonated 2D aluminosilicate can be formed and these protonated sites may be analogous to those in acid zeolites. Thereby, the 2D aluminosilicate shows its potential as a zeolite model. In this work, we studied water chemistry on 2D silica and aluminosilicate grown on a Pd(111) substrate by combining density function theory (DFT), thermal desorption spectroscopy (TDS), and ambient pressure photoelectron spectroscopy (AP-PES). We found that protonated 2D aluminosilicate on Pd(111) is thermally stable with both dehydrogenation and dehydration of the protonated surface energetically infeasible under 1000 K. Based on the theoretical and experimental results, once the aluminosilicate surface is protonated, no further water dissociation will take place. The AP-PES study suggests that molecular water can penetrates through the 2D bilayers and stays at the bilayer-substrate interface, leading to core-level shifts in the 2D bilayers due to changes of dipole moments. These findings show that the Brønsted acid sites on the Pd-supported 2D aluminosilicate are robust, and thereby provide fundamental information on the more complex zeolite surfaces.

12:00pm **SS+HC-WeM13 Double Layer Formation of Water Molecules on Graphene***, A. Akaishi, T. Yonemaru,* ***Jun Nakamura,*** The University of Electro-Communications (UEC-Tokyo), Japan

While graphite is known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as hydrocarbons on the surface are removed [1,2]. The contact angle estimated by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. On the other hand, water molecules have been confirmed to form layered structures on a graphene surface [4] and on the surface of carbon nanotubes [5]. But, the wettability of pristine graphene surfaces remains unsettled.

To investigate the water wettability of graphitic surfaces, we use molecular dynamics simulations of water molecules on the surface of a single graphene layer at room temperature [6]. The results indicate that a water droplet spreads over the entire surface and that a double-layer structure of water molecules forms on the surface, which means that wetting of graphitic surfaces is possible, but only by two layers of water molecules. No further water layers can cohere to the double-layer structure, but the formation of three-dimensional clusters of liquid water is confirmed. The surface of the double-layer structure acts as a hydrophobic surface. Such peculiar behavior of water molecules can be reasonably explained by the formation of hydrogen bonds: The hydrogen bonds of the interfacial water molecules form between the first two layers and also within each layer. This hydrogen-bond network is confined within the double layer, which means that no “dangling hydrogen bonds” appear on the surface of the double-layer structure. This formation of hydrogen bonds stabilizes the double-layer structure and makes its surface hydrophobic. Thus, the numerical simulations indicate that a graphene surface is perfectly wettable on the atomic scale and becomes hydrophobic once it is covered by this double layer of water molecules.

[1] Z. Li *et al.*, Nat. Mater. **12**, 925 (2013)

[2] A. Kozbial *et al.*, Carbon **74**, 218 (2014)

[3] T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Chem. Phys. B **107**, 1345 (2003)

[4] Y. Maekawa, K. Sasaoka, and T. Yamamoto, Jpn. J. Appl. Phys. **57**, 035102 (2018)

[5] Y. Homma *et al.*, Phys. Rev. Lett. **110**, 157402 (2013)

[6] A. Akaishi, T. Yonemaru, and J. Nakamura, ACS Omega **2**, 2184 (2017)

2D Materials Focus Topic
Room 201B - Session 2D+MN+NS+SS-WeA

IoT Session: Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Daniel Walkup, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park

2:20pm **2D+MN+NS+SS-WeA1 Impact of Hydrogen on Graphene-based Materials: Atomistic Modeling and Simulation of HRSTEM Images***, C. Guedj,* Univ. Grenoble Alpes, CEA, LETI, France*; L. Jaillet, F. Rousse,* ***Stéphane Redon,*** Univ. Grenoble Alpes, CNRS, INRIA, Grenoble INP*, LJK, France

The hydrogen energy transition is highly probable, because hydrogen is the most abundant element in the universe and represents an ideal “green” source of energy. Meanwhile, the safe hydrogen production and storage remains a major challenge still in progress. Potential production and storage materials include graphene. In terms of electronic and optoelectronic applications, hydrogen can tune the bandgap of graphene [1]. Hydrogen also plays a major role during the Chemical Vapour Decomposition (CVD) growth of graphene [2]. Hence, hydrogenated graphene-based materials are potentially relevant for various technological applications.

To understand and optimize the device efficiency and the interface engineering, it is advantageous to perform advanced nanocharacterizations, linked to numerical modelling and simulations. This task is particularly difficult, because hydrogen is labile and prone to rapid reorganization. This structural evolution may be monitored with transmission electron microscopy (TEM) techniques [3,4,5], but in spite of significant progresses, the direct detection of hydrogen with High Resolution Scanning Transmission Electron Microscopy (HRSTEM) or energy-loss spectroscopy still remains a serious challenge.

We investigate here the interaction of hydrogen with graphene using the Brenner module of the SAMSON software platform https://www.samson-connect.net and we propose an original methodology to characterize its structural arrangement at the atomic scale by simulating HRSTEM images to interpret experimental results. In particular, we compare the effect of hydrogen on dark field (DF), bright field (BF), high-angle annular dark filed (HAADF) and annular bright field (ABF) images, to estimate the best technique suited to hydrogen detection.

In addition, we present the effect of carbon vacancies and adatoms on the stability of hydrogen coverage, associated to the HRSTEM signatures of the most stable configurations. These results provide the necessary building blocks to analyze the structure and energetics of hydrogenated graphene-based materials at the atomic scale.

References

[1] Elias D C et al Science 323 610–3 (2009)

[2] Vlassiouk I et al., ACS Nano 5 6069–76 (2011)

[3] Beattie SD et al. Chem Commun 4448–4450 (2008)

[4] Ikeda K et al. Nanotechnology 20:204004 (2009)

[5] Muto S et al. J Appl Phys 105:123514 (2009)

2:40pm **2D+MN+NS+SS-WeA2 High Density H2 and He Plasmas: Can They be used to Treat Graphene?**, ***Hasan-Al Mehedi,*** Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France*; D. Ferrah,* Cea, Leti, Minatec, France*; J. Dubois, C. Petit-Etienne,* Laboratoire des Technologies de la Microélectronique, CNRS-UJF*; H. Okuno,* Cea, Inac/sp2m/lemma*; V. Bouchiat,* Institut Néel, CNRS-UJF-INP*; O.J. Renault,* CEA/LETI-University Grenoble Alpes, France*; G. Cunge,* Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France

Since graphene and other 2D materials have no bulk, a major issue is their sensitivity to surface contaminations, and the development of cleaning processes is mandatory. High density plasmas are attractive to treat (clean, dope, pattern) 2D materials because they are a mature industrial technology adapted to large area wafer. However, in these plasmas the substrate is bombarded by a high flux of both thermal radicals and reactive ions with typical energy above 10 eV, which can easily damage atomic layer thin materials. We have investigated systematically the interaction of H2 and He inductively coupled plasmas (ICP) with graphene in industrial reactors. We report a specific issue associated with the use of H2 plasma: they etch the inner part of plasma reactor walls, thus releasing impurities in the plasma, most notably O atoms that etch graphene and Si atoms which stick on it. The presence of parasitic oxygen presumably explains the discrepancies found in the literature regarding the impact of reactive plasmas on graphene damages. To get rid of this issue we propose to use a fluorinated aluminum chamber. In this case, fluorine atoms which are shown to be harmless to graphene are the only impurity in the plasma. Under such conditions H2 ICP plasma is shown to clean graphene without damages if the ion energy is kept below about 15 eV.

3:00pm **2D+MN+NS+SS-WeA3 Novel Binder-free $Ag@Ni(OH)_2$ over Graphene/Ni Foam and Glucose Sensing***,* ***Tong-Hyun Kang****, J.-S. Yu,* DGIST, Republic of Korea

Graphene combining with metal nanoparticles or other compounds is widely recognized to be a viable strategy to assemble high-activity catalysts.Unique properties of high conductivity and transparency, 2D morphology, and high stability in acid and alkaline solutions make graphene an excellent electron transfer medium on the interface of graphene/active materials as catalysts.Among them, graphene/metal nanoparticle (G/MNP) composites have been attracting more interest because of remarkably enhanced catalytic property, which is ascribed to a synergic effect from the interface of graphene and active sites. In general, reducing agents and electrodeposition methodshave been employed to *in-situ* reduce metal ions such as Au^{3+}, Pt^{4+}, Ag^{+}, and Cu^{2+} (M^{x+}) to MNPs on the graphene to form G/MNP composites.In this study, graphene is grown on nickel foam (NF) by chemical vapor deposition (CVD), which is directly used for MNP deposition. Different from bare NF, special phenomenon is observed that the graphene-coated nickel foam (GNF) composite can greatly speed up the electrodeless reduction of M^{x+} ions on the surface of the graphene. Interestingly, the MNP deposition and $Ni(OH)_2$ nanosheet assembly simultaneously occur on the GNF. Binder-free $Ni(OH)_2$-wrapped Ag hybrid developed on the GNF ($Ag@Ni(OH)_2$-GNF) is found to serve as an efficient electrochemical sensor because of its unique structure. A low detection limit of 0.3 μM and high sensitivity are achieved for the glucose detection, which confirms that the hierarchical electrode structure of $Ag@Ni(OH)_2$-GNF composite is highly effective to have extensive applications.

3:20pm **2D+MN+NS+SS-WeA4 Surface Modification and Magnetization of Carbon Based Nanostructures***,* ***Rina Tannenbaum,*** University of Stony Brook*; I.T. Kim,* Gachon University, Korea*; S. Sharma,* University of Stony Brook

We describe here a novel synthesis for the facile decoration of carbon nanomaterials (CNM) with monodisperse γ-Fe_2O_3 magnetic nanoparticles. These procedures were developed for multi-walled carbon nanotubes (MWNTs), reduce graphene (rGO) and reduced graphene nanoroses (rGO-roses). The decoration of these carbon nanomaterials with γ-Fe_2O_3 induces the magnetization of these structures and opens up the potential for their use in novel applications.

CNM/γ-Fe_2O_3 magnetic nanostructures were fabricated through a modified sol-gel process using ferric nitrate nonahydrate, $Fe(NO_3)_3\cdot 9H_2O$ as a starting material. Nucleation sites for the iron oxide were generated at the CNM surface due to the electrostatic interaction between Fe (III) ions and the carboxylate surface groups of acid-treated CNMs. The occurrence of gelation was inhibited by the addition of the NaDDBS surfactant, before the addition of propylene oxide, which is a gel promoter. The surfactant interfered in the growth stage of the iron oxide nanoparticles (gel phase) through to the coordinaton of the NaDDBS molecules to the iron (III) centers due to the attraction between the negatively-charged hydrophilic head of the surfactant and the positively-charged iron. The rGO-roses were further fabricated from decorated rGO via a novel emulsion process.

Various characterization methods were used to confirm the formation of well-defined maghemite nanoparticles, and show that they were tethered to the walls of the CNMs. The tethered γ-Fe_2O_3 nanoparticles imparted magnetic characteristics to the CNMs, which in turn, became superparamagnetic. The magnetic carbon nanotubes and magnetic rGO were introduced into a polymer matrix [#] and were oriented parallel to the direction of an externally-applied magnetic field. The anisotropic nanocomposites were then used as anodes in lithium ion batteries. The magnetic rGO-roses were used as nuclear magnetic resonance contrast material.

4:20pm **2D+MN+NS+SS-WeA7 Chemical Modification of Graphene and Carbon Nano Tubes as viewed by XPS and NEXAFS Spectroscopies underpinned by DFT Spectra Simulation***, C. Ehlert, E. Donskyi,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; P.L. Girard-Lauriault,* McGill University, Canada*; R. Illgen,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Lippitz,* Bundesanstalt für Materialforschung und -prüfung (BAM)*; R. Haag, M. Adeli,* Freie Universität Berlin, Germany*;* ***Wolfgang Unger****,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Graphene is a two-dimensional carbon network with unique properties. However, its low solubility, poor reactivity and the limited accessibility of a well-defined basal plane are major challenges for applications. An ideal method to overcome these problems is the covalent attachment of functional molecules to its surface which enable further reactive modifications for specific applications. There are several technologies for surface functionalization of graphene and related CNT materials. To get control on the functionalization process and to optimize the performance of the modified surfaces analytical tools for surface chemical characterization are required. X-ray absorption (NEXAFS) and photoelectron spectroscopy (XPS) have been identified to be rather powerful here [1-3]. Specifically, NEXAFS spectroscopy underpinned by quantum chemical spectrum simulations [4] is unique in a way to address changes of aromaticity and defect formation at the graphene surface during functionalization.

For relevant surface modification technologies, we present examples on how NEXAFS and XPS are fit for purpose. All presented modifications aim on the production of platforms for defined functional 2D nanomaterials, as for example multi-functional hybrid architectures. In detail we investigated:

- A wet chemical method for covalent functionalization of graphene sheets by a one-pot nitrene [2+1] cycloaddition reaction under mild conditions. Here a reaction between 2,4,6-trichloro-1,3,5-triazine and sodium azide with thermally reduced graphene oxide (TRGO) results in defined dichlorotriazine-functionalized graphene sheets.
- Graphene and carbon nanotube functionalized by Vacuum-Ultraviolet (VUV) induced photochemical or r.f. cw low pressure plasma processes to introduce amino, hydroxy or brominated functionalities.

To underpin finger-print information delivered by C K-edge NEXAFS we studied the effects of selected point and line defects as well as chemical modifications for a single graphene layer model by density functional theory based spectrum simulations.

Acknowledgement

We acknowledge support by the team at the BESSY II synchrotron radiation facility in Berlin, Germany, as well as Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group.

References

[1] P.-L. Girard-Lauriault et al., Appl. Surf. Sci., 258 2012 8448-8454, DOI: 10.1016/j.apsusc.2012.03.012

[2] A. Lippitz et al., Surf. Sci., 611 2013 L1-L7, DOI: 10.1016/j.susc.2013.01.020

[3] A. Faghani et al., Angew. Chemie (International ed.), 56 2017 2675-2679, DOI:10.1002/anie.201612422

[4] C. Ehlert, et al., Phys.Chem.Chem.Phys., 16 2014 14083-14095, DOI: 10.1039/c4cp01106f

4:40pm **2D+MN+NS+SS-WeA8 Elastic Spongy Graphene-Functionalized Silicon Anode with Excellent Cycle Stability in Li battery***,* ***Byong-June Lee****, J.-S. Yu,* DGIST, Republic of Korea

Graphite plays a prominent role as a typical anode material in the lithium ion batteries (LIBs) because of its high lithiation-dilithiation reversibility and low voltage window. Unfortunately, the capacity is limited to 372 mAh g^{-1}[1,2]. To search for materials with higher lithium storage capacity, a great number of investigations on metal oxides (or sulfides), Sn, P, and Si have been carried out in recent decades. Among these materials, silicon can make alloy with lithium in the form of $Li_{22}Si_5$ to deliver a highest theoretical gravimetric capacity of ~4200 mAh g^{-1}, and thus is considered to be one of the most promising anode materials for next generation LIB. It is worth mentioning that its quite low delithiation potential and high lithium storage capacity can provide a wide working voltage window and energy density, which enable promising potential application in electric vehicles. However, those advantages are seriously offset by a great challenge of large volume expansion during lithiation process and the resultant breakage of bulk silicon particles and solid electrolyte interface (SEI), which causes a serious damage to the electrode structure and thus gives rise to a fast decay of the specific capacity [3].

In this work, novel 3D spongy grapheme (SG)-functionalized silicon is for the first time demonstrated by chemical vapor deposition for a LIB anode, which can overcome the common silicon anode issues such as poor conductivity and volume expansion of Si as well as transfer of Li ion towards the Si. The elastic feature of graphene has excellent function to self-adaptively buffer the volume variation during charge-discharge process. In particular, different from traditional graphene or carbon shells (core-shell and yolk-shell), the spongy 3D graphene networks provide much improved unique functions with excellent long-cycle stability and rate capability. The Si@SG electrode exhibits excellent cycling performance with high reversible specific capacity [4]. A superior 95% capacity retention is achieved after 510 cycles. All the electrochemical performances get benefits from the well-designed functional SG shells, where interconnected nano-graphene structure not only guarantees a high conductive network but also provides more free paths for excellent mass transfer in addition to self-adaptive buffering capability .

Reference s :

[1] B. Fang, J. H. Kim, M.-S. Kim, J.-S. Yu, Acc. Chem. Res. 46(2013) 1397-1406.

[2] C. Zhang, J.-S. Yu, Chem. Eur. J. 22 (2016) 4422-4430.

[3] M. Zhou, X. Li, B, Wang, Y, Zhang, et al. Nano Lett. 15(2015) 6222-6228.

[4] C.Zhang, T.-H. Kang, J.-S. Yu, Nano Research, 11(2018) 233-245.

5:00pm **2D+MN+NS+SS-WeA9 Electrical and Structural Changes of Multilayer WSe_2 Transistors: Atmospheric Gas Adsorption and Long Term Aging***,* ***Anna Hoffman****, M.G. Stanford, C. Zhng,* University of Tennessee Knoxville*; I. Ivanon,* Oak Ridge National Laboratory*; A.D. Oyedele, D.G. Mandrus,* University of Tennessee Knoxville*; L. Liang, B.G. Sumpter, K. Xiao,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville

Interest in transition metal dichalcogenides (TMDs) for opto-electronic applications has been growing recently due to their unique properties and layered structure. Surface science and DFT simulations have corroborated p-type doping and n-type suppression of O_2 and H_2O adsorption in TMDs however, electrical characterization has not been fully investigated. This presentation will demonstrate the reversible suppression of n-type conduction in ambi-polar WSe_2 via water adsorption, which logically has a larger impact as the WSe_2 thickness decreases. Additionally, we observe a reversible and irreversible n-type suppression and p-type doping which we attribute to H_2O adsorption and isoelectronic oxygen chemisorption, respectively, at chalcogen vacancies during long term aging in atmosphere over 6 weeks. Finally, controlled oxygen plasma exposure is utilized to oxidize and p-type dope WSe_2. We will overview our device fabrication and electrical testing procedure, and transfer characteristics for our as-fabricated devices for various WSe_2 thicknesses in air and in vacuum will be illustrated. Long-term (6 week) electrical measurements in both air and vacuum are compared to the as-fabricated devices. Finally, complementary atomic force microscopy and Raman Spectroscopy are used to characterize the devices

5:20pm **2D+MN+NS+SS-WeA10 Ion Migration Studies in Exfoliated 2D Molybdenum Oxide via Ionic Liquid Gating for Neuromorphic Device Applications***,* ***Cheng Zhang****, P.R. Pudasaini, A.D. Oyedele,* University of Tennessee Knoxville*; A.V. Ivelev, K. Xiao, T.Z. Ward,* Oak Ridge National Laboratory*; D.G. Mandrus,* University of Tennessee Knoxville*; O.S. Ovchinnikova,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville

The formation of an electric double layer in ionic liquid (IL) can electrostatically induce charge carriers and/or intercalate ions in and out of the lattice which can trigger a large change of the electronic, optical and magnetic properties of materials and even modify the crystal structure. We present a systematic study of ionic liquid gating of exfoliated 2D molybdenum trioxide (MoO_3) devices and correlate the resultant electrical properties to the electrochemical doping via ion migration during the IL biasing process. A nearly nine orders of magnitude modulation of the MoO_3 conductivity is obtained for the two types of ionic liquids that are investigated. In addition, notably rapid on/off switching was realized through a lithium-containing ionic liquid whereas much slower modulation was induced via oxygen extraction/intercalation. Time-of-Flight Secondary Ion Mass Spectrometry confirms the Li intercalation. Results of short-pulse tests show the potential of these MoO_3 devices as neuromorphic computing elements due to their synaptic plasticity.

5:40pm **2D+MN+NS+SS-WeA11 Infrared Absorption of Nanometer-scale Thermally Reduced Graphene Oxide*, Erin Cleveland*,** *J. Nolde, G. Jernigan, E. Aifer,* U.S. Naval Research Laboratory

Strong optical absorption is of fundamental importance to infrared (IR) sensors, and it has been well established that graphene is one of the strongest IR absorbing materials, with approximately 2.3% absorption in the IR and visible regions for a single layer. While reduced graphene oxide (RGO) may not have quite the same absorption strength as graphene on a layer-by layer basis, we believe that by controllably reducing the oxygen concentration within the GO films we can increase the absorption of the RGO film to approach that of graphene. RGO films, unlike graphene, however, can be made arbitrarily thick, allowing for much higher absorbance in a single pass. Here we explore the use of GO films of varying thickness and UHV annealing temperature to achieve near 100% midwave IR absorbance in a quarter-wave reflection filter structure consisting of an RGO film on top of a λ/4-thick SiO_2 layer deposited over a Ti/Pd mirror.

Graphene oxide (GO) is a two-dimensional network consisting of a graphene basal plane decorated with oxygen moieties in the forms of carbonyls, epoxies and hydroxyl groups resulting in variable number of *sp*^{2}and *sp*^{3}bonding geometries. Theory indicates that GO bandstructure and transport are strongly dependent on the ratio of the *sp*^{2} and *sp*^{3} bonding fractions, and therefore, by controllably removing specific oxygen groups, one can tune its electronic, optical, and chemical properties. While it is difficult to modify the oxygen concentration using wet chemical processing, e.g. using hydrazine, GO can be thermally reduced in H_2-N_2 forming gas with more precise control. However, this procedure, like chemical reduction promotes the occurrence of N and H impurities, as well as carbon vacancies within the graphene basal plane, significantly degrading the electronic quality of the film. Here, we use ultrahigh vacuum ($<10^{-9}$ Torr) annealing to controllably reduce the oxygen concentration in GO films while introducing fewer defects. Not only does UHV annealing prevent the introduction of impurities, but after oxygen removal, dangling bonds tend to reform in hexagonal structure. UHV annealing also enables in-vacuo measurement by x-ray photoelectron spectroscopy (XPS) to precisely characterize the overall oxygen concentration and its distribution within alcohol, epoxy and carbonyl species. Following an 800°C UHV anneal for example, we find that the oxygen concentration is reduced to ~5%, and the layer spacing is equivalent to epitaxial graphene grown on the C-face of SiC.

6:00pm **2D+MN+NS+SS-WeA12 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers and their application in All-Carbon Capacitors*, Xianghui Zhang*,** *P. Penner, E. Marschewski,* Bielefeld University, Germany*; T. Weimann, P. Hinze,* Physikalisch-Technische Bundesanstalt, Braunschweig, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials that are made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous studies of the charge transport in molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaIn) top-electrodes[1] and conductive probe atomic force microscopy (CP-AFM)[2]. Additional investigations of the dielectric properties of pristine SAMs and CNMs were performed by impedance spectroscopy on EGaIn tunneling junctions. Here we demonstrate the fabrication and characterization of all-carbon capacitors (ACCs) composed of multilayer stacks of dielectric CNMs that are sandwiched between two types of carbon-based conducting electrodes: (1) trilayer graphene made by chemical vapor deposition and mechanical stacking; (2) pyrolyzed graphitic carbon (PGC) made by pyrolysis of cross-linked aromatic molecules. The junction area is defined by the width of electrode ribbons, ranging from 1 to 2500 µm^2, and the separation between two electrodes is tuned by the number of CNM layers. The frequency response of nanocapacitors was measured with an LCR meter. A dielectric constant of 3.5 and a capacitance density of up to 0.5 µF/cm^2 were derived from the junction capacitance. A dielectric strength of 6.2 MV/cm was determined. These results show the potential of carbon nanomembranes to be used as dielectric components in next-generation environment-friendly carbon-based molecular electronic devices.

[1] P. Penner, X. Zhang, E. Marschewski, F. Behler, P. Angelova, A. Beyer, J. Christoffers, A. Gölzhäuser, *Journal of Physical Chemistry C*, 2014, 118, 21687.

[2] X. Zhang, E. Marschewski, P. Penner, A. Beyer and A. Gölzhäuser, *Journal of Applied Physics*, 2017, 122, 055103.

Biomaterial Interfaces Division
Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials*, David G. Castner*[1]*,*** University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials*, Keith A. Brown*[2]*,*** Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

---

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

[2] **Future Stars of the AVS**

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications***, **Mark Losego**[1],* Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO_2/Au(111)***, **Ashleigh Baber**[2], D.T. Boyle, J. Wilke, V. Lam, D. Schlosser,* James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO_2/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x ($x<2$). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO_2/Au(111). The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View***, **Gareth Parkinson**[3],* TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through ”single atom” active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium***, **Olga Ovchinnikova**[4],* Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes***, **Rebecca Abergel**[5],* Lawrence Berkeley Lab, University of California, Berkeley*; G. Deblonde, A. Mueller, P. Ercius,* Lawrence Berkeley National Laboratory*; A.M. Minor,* Lawrence Berkeley Lab, University of California, Berkeley*; C.H. Booth, W.A. de Jong,* Lawrence Berkeley National Laboratory*; R. Strong,* Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular

---

[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Future Stars of the AVS**

[5] **Future Stars of the AVS**

weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces***, **Liney Arnadottir**[1], L.H. Sprowl,* Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+SS-WeA

Wide and Ultra-Wide Bandgap Materials for Electronic Devices: Growth, Modeling and Properties

Moderators: Erica Douglas, Sandia National Laboratories, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:40pm **EM+2D+SS-WeA2 2300 V Reverse Breakdown Voltage Ga_2O_3 Schottky Rectifiers***, **Jiancheng Yang**[2], F.R. Ren,* University of Florida*; M.J. Tadjer,* U.S. Naval Research Laboratory*; S.J. Pearton,* University of Florida*; A. Kuramata,* Tamura Corporation and Novel Crystal Technology, Inc., Japan

A reverse breakdown voltage of 2300 V with corresponding breakdown field of 1.15 MV/cm was demonstrated for 20 µm epi-β-Ga_2O_3 edge-terminated vertical Schottky rectifiers. This breakdown voltage is the highest ever reported for Ga_2O_3 rectifiers. Ga_2O_3 has an energy band gap of range 4.5 – 4.9 eV, which correlates to the theoretical breakdown electric field of ~8 MV/cm. The theoretical Baliga figure of merit (defined as V_B^2/R_{ON}, where V_B is the reverse breakdown voltage and R_{ON} is the on-state resistance) of Ga_2O_3 estimated to be 400% higher than GaN.[1] Previously reported, an unterminated Ga_2O_3 rectifier shown a breakdown voltage of 1600 V, and a field-plated Schottky diode has a breakdown voltage of 1076 V with the epi thickness 7 µm [2,3] This work has shown the improvement of the Ga_2O_3 vertical rectifiers breakdown voltage using a field-plate terminated approach with a lightly doped 20 µm Ga_2O_3 epitaxial layer . The edge-terminated Schottky rectifiers of various dimensions (circular geometry with diameter of 50-200 µm and square diodes with areas 4×10^{-3}- 10^{-2} cm^2) fabricated on 20µm lightly doped (n=2.10×10^{15} cm $^{-3}$) β-Ga_2O_3 epitaxial layers grown by hydride vapor phase epitaxy on conducting (n=3.6 $\times 10^{18}$ cm^{-3}) Ga_2O_3 substrates grown by edge-defined, film-fed growth. The R_{ON} for these devices was 0.25 Ω-cm^2, leading to a figure of merit (V_B^2/R_{ON}) of 21.2 MW/cm^2. The Schottky barrier height with the Ni/Au based metallization was 1.03 eV, with an ideality factor of 1.1 at room temperature. The Richardson's constant of 43.35 A/cm-K^2 was extracted from the temperature dependent forward IV. The breakdown voltages for the different size devices ranged from 1400-2300V, with a general, but not a linear trend of decreasing breakdown voltage for larger area rectifiers. The diode reverse recovery time of ~22 ns was measured by switching the diode from +2V to -2V.

1. J. Green, K. D. Chabak, E. R. Heller, R. C. Fitch, M. Baldini, A. Fiedler, K. Irmscher, G. Wagner, Z. Galazka, S. E. Tetlak, A. Crespo, K. Leedy, and G. H. Jessen, IEEE Electron Device Lett., vol. 37, no. 7, pp. 902–905, Jul. (2016)
2. J. Yang, S. Ahn, F. Ren, S. J. Pearton, S. Jang, and A. Kuramata, IEEE Electron Device Lett,. 38(7), 906 (2017).
3. K. Konishi, K. Goto, H. Murakami, Y. Kumagai, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, Appl. Phys. Lett. 110, 103506 (2017).

3:00pm **EM+2D+SS-WeA3 Characterization of β-$(Al,Ga,In)_2O_3$ Epitaxial Films for UV Photodetector Applications***, **Luke Lyle**, L.M. Porter, R. Davis,* Carnegie Mellon University*; S. Okur, G.S. Tompa,* Structured Materials Industries, Inc.*; M. Chandrashekhar, V. Chava, J. Letton,* University of South Carolina

β-Ga_2O_3 has garnered increased attention over the last few years due to its ultra-wide bandgap of ~5.0 eV and the ability to grow Ga_2O_3 single crystals from the melt. In addition to its desirability for high power electronics, Ga_2O_3 is well suited for solar-blind UV photodetectors. These detectors are coveted by numerous industries and the military for applications ranging from flame- and missile-plume detection to ozone hole monitoring. In this study we have grown $(Al,Ga,In)_2O_3$-based alloy epitaxial films on sapphire via metalorganic chemical vapor deposition (MOCVD) to investigate their potential application for wavelength-tunable UV photodetectors. The films were characterized structurally, optically, and chemically using x-ray diffraction (XRD), optical transmittance, and energy dispersive x-ray spectroscopy (EDX). Based on XRD and EDX results, β-$(Al_xGa_{1-x})_2O_3$, β-$(In_xGa_{1-x})_2O_3$, and β-Ga_2O_3 epitaxial films with compositions through x = 0.29 (for Al) and x = 0.13 (for In) were grown. The optical bandgap was found to correspondingly vary between 5.5±0.1 and 4.3±0.3 eV, as a function of composition. MSM- and Schottky-based solar-blind UV photodetectors were also fabricated on selected films. The devices showed responsivities up to 1E5 A/W and quantum efficiencies up to 6E5 at 220 nm from a deuterium lamp. The wavelength tunability of the photodetectors is currently being investigated and will be discussed in this presentation.

3:20pm **EM+2D+SS-WeA4 High Three-terminal Breakdown Voltage Quasi-two-dimensional β -Ga_2O_3 Field-effect Transistors with a Dual Field Plate Structure***, **Jinho Bae**,* Korea University, Republic of Korea*; H.W. Kim, I.H. Kang,* Korea Electrotechnology Research Institute (KERI), Republic of Korea*; G.S. Yang, S.Y. Oh, J.H. Kim,* Korea University, Republic of Korea

β-Ga_2O_3 is an intriguing material because of its large direct bandgap (4.85 eV), high breakdown field (~8 MV/cm) and excellent thermal and chemical stability. Baliga's figure of merit of β-Ga_2O_3 is 3214.1, superior to those of other materials such as GaN (846.0) or SiC (317.1). Although β-Ga_2O_3 is not a van der Waals material, β-Ga_2O_3 can be mechanically exfoliated from single crystal substrate into thin layer due to the large anisotropy of the unit cell. Quasi-2D β-Ga_2O_3 devices shows superior electrical properties and robustness in harsh environment, which shows potential of β-Ga_2O_3 as nanoscale power devices. However, quasi-2D β-Ga_2O_3 power devices show premature breakdown due to the electric field concentration. Adopting multiple field plates to relieve the electric field concentration and prevent premature breakdown greatly enhance the performance of power devices, which can be applied to β-Ga_2O_3 nanoelectronic power devices.

H-BN has been used as a dielectric material of 2D devices due to its excellent thermal conductivity and high dielectric constant, as well as atomically flat surface, which can be obtained through mechanical exfoliation. In our work, we used h-BN as a gate field plate dielectric layer by selective transfer on β-Ga_2O_3 channel using PDMS film. SiO_2 dielectric layer was deposited on devices followed by metal deposition for source field plate structure. By applying dual field plate structure, β-Ga_2O_3 devices can show excellent performance in high voltage condition.

β-Ga_2O_3 MESFETs with h-BN gate field plate were fabricated by using the β-Ga_2O_3 and h-BN flakes obtained from respective crystals. Ohmic metal was deposited on mechanically exfoliated β-Ga_2O_3 flakes, followed by precise positioning of exfoliated h-BN flakes on the channel. Gate field plate was fabricated with a part of the electrode overlapped with h-BN. Dual field plate structure was fabricated after deposition of SiO_2 and source field plate metal. Fabricated devices showed excellent output and transfer characteristics even after one month storage, which shows excellent air-stability. Three-terminal off-state breakdown voltage of fabricated device was measured, which shows improvement in breakdown voltage. The electric field distribution was calculated by Silvaco Atlas framework to

---

[1] **Future Stars of the AVS**

[2] **National Student Award Finalist**

study the effect of dual field plate on electric field, which explains the improvement of breakdown voltage in those structure. In this study, we present that the performance of β-Ga_2O_3 MESFET as a power device can be improved by adopting dual field plate structure, paving a way to the high-power nanoelectronic β-Ga_2O_3 devices. The details of our work will be discussed in the conference.

4:20pm **EM+2D+SS-WeA7 GaN Vertical Device Technology and its Future**, *S.C. Chowdhury,* ***Dong Ji,*** UC Davis **INVITED**

Vertical GaN devices are ideal for high power applications owing to their wide bandgap-originated material properties, similar to SiC. What makes GaN vertical devices more attractive than SiC, is the capability to offer bulk regions with electron mobility over 1200cm^2/V·sec. Due to higher carrier mobility made possible by superior growth techniques, the figure of merit offered by GaN diodes or FETs is higher compared to SiC counterparts. From TCAD drift diffusion simulation we have shown the advantage of GaN devices become rapidly significant over SiC diodes at higher voltages. In our experimental studies we have successfully demonstrated transistors blocking over 1.4kV.

In this presentation, we will go over various types of vertical devices for power conversion that we are pursuing in our group and go over the achievements and challenges in each.

CAVETs were the first vertical devices[1] that demonstrated the potential of GaN in these technology. CAVETs are realized with Mg-ion implanted [2] current blocking layers (CBLs) with regrown channel. Alternatively they can have Mg-doped CBLs with a regrown channel layer on a trench. In our trench CAVETs we have successfully blocked up to 880V with an R_{on} less than 2.7milli-ohm cm^2.

To date, most successful results in GaN vertical devices have come out of MOSFETs, which traditionally rely on inversion channels. MOSFETs with an un-doped GaN interlayer as a channel and in-situ MOCVD oxide, called OG-FET have demonstrated superior performance with low specific on-state resistance (R_{on}) Over 1.4kV blocking with an R_{on} less than 2.2milli-ohm cm^2 was recently demonstrated by our group where the role of channel mobility got highlighted[3].

One of common issue in all these devices is the realization of a robust buried p-n junction, which we will also go over along with other challenges faced by each of these device types and discuss paths to overcome those.

1. S. Chowdhury, M. H. Wong, B. L. Swenson, and U. K. Mishra, IEEE Electron Device Letters **33**, 41 (2012).
2. S. Mandal, A. Agarwal, E. Ahmadi, K. M. Bhat, D. Ji, M. A. Laurent, S. Keller, and S. Chowdhury, IEEE Electron Device Letters, **38**, 7 (2017)
3. D. Ji, C. Gupta, S. H. Chan, A. Agarwal, W. Li, S. Keller, U. K. Mishra, and S. Chowdhury, *International Electron Devices Meeting, IEDM*, 2017

5:00pm **EM+2D+SS-WeA9 Effects of Proton Irradiation Energy on SiN_x/AlGaN/GaN Metal-insulator-semiconductor High Electron Mobility Transistors**, ***Chaker Fares,*** *F.R. Ren,* University of Florida*; J.H. Kim,* Korea University, Republic of Korea*; S.J. Pearton,* University of Florida*; C.F. Lo, J.W. Johnson,* IQE*; G.S. Yang,* Korea University, Republic of Korea

The effects of proton irradiation energy ranging from 5 to 15 MeV on the electrical properties of SiNx/AlGaN/GaN metal-insulator-semiconductor high electron mobility transistors (MISHEMTs) using in-situ grown silicon nitride as the gate dielectric were studied. In applications such as satellite-based communication, remote sensing, radar technology, and nuclear energy production, microelectronics that are resistant to radiation must be utilized. Of the many materials and device architectures previously investigated, AlGaN/GaN high electron mobility transistors (HEMTs) show significant potential for environments where radiation hardness, elevated temperature, and high-power operation are required. Although several studies have been performed to analyze how HEMTs respond to irradiation damage, data on the effects of proton irradiation energy on MISHEMTs are scarce. In this study, AlGaN/GaN MISHEMT samples were irradiated at various proton irradiation energies at a fixed dose of 2.5×10^{14} cm^{-2} to determine the effects on device performance. After proton irradiation, all devices were functional and showed minimal degradation compared to previous reports of HEMTs irradiated at similar conditions.The dc saturation current was reduced by 10.4, 3.2 and 0.5% for MISHEMTs irradiated with proton energies of 5, 10, and 15 MeV, respectively. Device performance degradations were more pronounced in the irradiated samples under high-frequency operation. At a frequency of 100 KHz, the saturation drain current reduction at a gate voltage of 3 V was 40%, 19% and 17% after proton irradiation at 5, 10, and 15 MeV, respectively. At higher duty cycles, the drain current reduction is less severe. The results of this study demonstrated the device reliability of AlGaN/GaN MISHEMTs in environments where a resilience to radiation is required.

5:20pm **EM+2D+SS-WeA10 Cesium-Free III-Nitride Photocathodes Based on Control of Polarization Charge**, ***Douglas Bell,*** Jet Propulsion Laboratory, California Institute of Technology*; E. Rocco, F. Shahedipour-Sandvik,* SUNY Polytechnic Institute*; S. Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

III-nitride photocathodes are well-suited for ultraviolet (UV) detection, with commercial, defense, and astronomical applications. Photocathodes detect light by absorbing photons which create electron-hole pairs, and emitting those electrons into vacuum, where they are detected and amplified by a gain-producing device such as a microchannel plate. This type of device is capable of ultra-low dark current and enables photon counting. The wide bandgaps available in the AlGaN family provide intrinsic solar blindness, and the long-wavelength cutoff may be tuned by control of composition.

Among other properties, negative electron affinity (NEA) is desirable for these structures in order to maximize quantum efficiency (QE), or the number of electrons emitted per incident photon. Normally surface cesiation is used to create low or negative electron affinity of the GaN photocathode surface; however, the resulting highly reactive surface must be protected from air during fabrication and use, necessitating a sealed-tube configuration. Even so, the reactive surfaces of these devices cause degraded performance over time. Cesium-free photocathodes would offer lower cost, smaller size and mass, improved robustness, and greater chemical stability, in addition to the major advantages of higher QE and longer lifetimes.

We will report on the use of polarization engineering in order to achieve high QE without the use of Cs. We will discuss progress in design, fabrication, and characterization of polarization-engineered III-nitride photocathodes. An important component of these designs is the use of N-polar GaN and AlGaN. The nitride polarity affects the interface and surface polarization charge, and the ability to achieve low electron affinity depends critically on control of this charge. Designs using polarization charge engineering also enable optimization of the near-surface potential to further increase QE. We will describe the growth challenges of N-polar GaN and AlGaN and its implementation in photocathode devices. We will present results demonstrating high (>15%) QE for non-cesiated N-polar GaN photocathodes, with a clear path toward higher efficiency devices.

5:40pm **EM+2D+SS-WeA11 Current Enhancement for Ultra-Wide Bandgap AlGaN High Electron Mobility Transistors by Regrowth Contact Design**, ***Erica Douglas,*** *B. Klein, S. Reza, A.A. Allerman, R.J. Kaplar, A.M. Armstrong, A.G. Baca,* Sandia National Laboratories

Recently, ultra-wide bandgap (UWBG) materials, such as Al-rich AlGaN with bandgaps approaching 6 eV, are being investigated to drive high-power electronic applications to even higher voltages, due to increased critical electric field compared to wide bandgap materials, such as GaN.[1] However, challenges have been encountered with Al-rich AlGaN, and in particular an increase in contact resistance as the bandgap for heterostructures increases.[2] High contact resistance ultimately limits the performance that can be achieved for these novel heterostructure-based devices, as source and drain resistances can be dominated by Ohmic contacts. While planar metal stacks with a rapid thermal anneal have shown some level of success, a complimentary approach using doped regrowth for the Ohmic contact regions with materials of lower bandgap has also shown a potential path for lowering contact resistance.[2] Our work explores regrown Ohmic contacts composed of lower bandgap Si-doped GaN to $Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ heterostructures , achieving a maximum saturated drain current of ~ 45mA/mm. Additionally, we demonstrate the ability to increase the saturated drain current almost 3X (from ~45 mA/mm to ~130 mA/mm) for UWBG HEMTs through a circular perforation design as well as a comb-type structure by means of regrowth contact design engineering.

[1] R. J. Kaplar, *et. al*, “Review—Ultra-Wide-Bandgap AlGaN Power Electronic Devices,” ECS J. Solid State Sci. Technol., vol. 6, no. 2, pp. Q3061-Q3066, Jan. 2017.

[2] B. A. Klein, *et. al*, “Planar Ohmic Contacts to $Al_{0.45}Ga_{0.55}N/Al_{0.3}Ga_{0.7}N$ High Electron Mobility Transistors,” ECS J. Solid State Sci. Technol., vol. 6, no. 11, pp. S3067-S3071, Aug. 2017.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results

and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

6:00pm **EM+2D+SS-WeA12 Understanding Homoepitaxial GaN Growth***, **Jennifer Hite**, T.J. Anderson, M.A. Mastro, L.E. Luna, J.C. Gallagher, J.A. Freitas,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

The availability of high quality, free-standing GaN substrates opens windows for new device applications in III-nitrides, especially in vertical structures. With the introduction of these native substrates, the properties of nitrides are no longer dominated by defects introduced by heteroepitaxial growth. However, additional materials challenges are coming to the forefront that need to be understood and surmounted in order to allow homoepitaxial devices to achieve their full potential.

In order to enable device-quality epitaxial layers, a deeper understanding of substrate preparation and the effects of the substrate and growth initiation on the characteristics of the epitaxial layers is required for metal organic chemical vapor deposition (MOCVD) growth of homoepitaxial films. We investigate these effects on epi morphology, uniformity, and impurity incorporation at the interface and in the films. Although the initial substrate factors influencing the epi can be subtle, they can have far reaching impact on device performance. Additionally, the interface between substrate and epitaxy is examined to enable reduction of unintentional impurity incorporation, especially Si, at this surface. By studying these effects using wafers from several different vendors, with substrates from both hydride vapor phase epitaxy (HVPE) and ammonothermal techniques, an understanding of the requirements for device quality MOCVD homoepitaxy can be determined.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeA

Theory and Dynamics of Heterogeneously Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

2:20pm **HC+SS-WeA1 Online Kinetics Study of Oxidative Coupling of Methane over La_2O_3 for C_2 Activation: What is Behind the Distinguished Light-off Temperatures***, **Yong Yang**, Z. Liu, E.I. Vovk, X. Zhou, C. Guan,* ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C_2 products (ethane and ethylene). The main difficulties from further investigation of this reaction are due to the nature of its high temperature and reaction exothermicity. In this work, a specially designed online characterization setup is applied for this reaction, which achieved both precise bed temperature control and real time product measurement. The setup combines a micro reactor and realtime mass spectroscopy. The reaction was performed under simulated industrial condition. For the first time, the Arrhenius plots of the major OCM products (CO_2, ethane and ethylene) were obtained, and their temperature dependence as well as the respective activation energy barriers were clearly differentiated, over a recently reported high performance nanorod La_2O_3 catalyst. Different from general expectation, CO_2, the fully oxidized carbon species, dominates all the products in the lower temperature region, and less oxidized C_2 species are only formed at much higher temperatures. Further analysis of the Arrhenius plots indicates that selectivity and apparent activation energy for both CO_x and C_2 products are strongly influenced by the oxygen concentration and temperature. Combined with density functional theory calculations and additional experimental measurements, significant insights are brought to this high temperature reaction of wide interest. Furtheranalysis specially focusing on this temperature region, applying XPS surface studies with *in-situ* high pressure cell and XRD bulk structure with *operando* reactor, revealed that there are both intermediates and poisoning species formation. With these new experiment results with distinguished lights-off products temperature provide new insights for understanding OCM reaction.

2:40pm **HC+SS-WeA2 Surface Reactivity of Activated CO_2***, **Richard van Lent**[1],* Leiden University, Netherlands*; A.J. Walsh, M.A. Gleeson,* DIFFER, Netherlands*; L.B.F. Juurlink,* Leiden University, Netherlands

Catalytically converting CO_2 into renewable fuels is a promising avenue that addresses the current fuel and energy storage challenges. Depending on the process, conversion of CO_2 may involve initial breaking of the OC=O bond. If so, this highly endothermic step is likely rate limiting to the overall process. Ultra–high vacuum (UHV) research on well-defined surfaces can provide fundamental insight into such processes, e.g. how dissociation may be aided by internal energy in CO_2, the metal's identity and the surface structure.

Internal energy has been shown to promote the highly activated dissociative adsorption of CO_2 on Ni(100) [1]. Rovibrationally state-resolved measurements for CH_4 on Ni(100) have shown that excitation of the ν_3 antisymmetric stretch vibration has a promoting effect that approximately equals kinetic energy for Ni(100) surfaces [2,3]. For other metal surfaces and CH_4 vibrations, the relative efficacy of vibrational and kinetic energies varies between 0.4 and 1.4 [2].

To start unravelling how CO_2 dissociates on a surface, we combine standard supersonic molecular beam techniques with high resolution continuous wave (cw) IR laser excitation. We study the effect of ν_3 antisymmetric stretch excitation of CO_2 on dissociative adsorption on a Ni(711) surface.

For excitation, we use a 3.9-4.6 µm single mode optical parametric oscillator (OPO). The OPO is frequency-stabilized by locking onto the derivative of the lamb dip of the specific rovibrational transition of interest. Frequency-stabilized IR radiation is crossed with a supersonic molecular beam that impinges onto the cleaned Ni(711) surface under UHV conditions. We use methods to determine absolute reactivities for CO_2 molecules with and without laser excitation. We extract rovibrational state-dependent absolute sticking probabilities as a function of kinetic energy. From this data, we determine the relative efficacy of vibrational and kinetic energy in overcoming the large activation barrier to dissociation.

[1] M. P. D'Evelyn, A. V. Hamza, G. E. Gdowski, and R. J. Madix, *Surf. Sci.***167**, 451 (1986).

[2] L. B. F. Juurlink, D. R. Killelea, and A. L. Utz, Prog. Surf. Sci. **84**, 69 (2009).

[3] B. L. Yoder, R. Bisson, and R. D. Beck, Sci. **329** , 553 (2010).

3:00pm **HC+SS-WeA3 Shining Light on Complexity: State- and Energy-Resolved Studies of Gas-Surface Reaction Dynamics and Mechanism***, **Arthur Utz**,* Tufts University **INVITED**

Gas-surface reactions on a metal surface can be far more complex than their net chemical equation would suggest. The heterogeneity of the surface, and its ability to restructure, impact the availability and energetics of reaction sites, energy redistribution processes triggered by the gas-surface collision dictate transition state access, and many coupled chemical processes can influence the reaction's outcome.

The talk will survey the ability to vibrational state selected measurements of gas-surface reactivity to systematically unravel important aspects of this complexity and provide molecular-level mechanistic insights that can guide our understanding and predictions about these processes. The experiments use infrared light to excite a single quantum rotational and vibrational level of the gas-surface reagent molecule and a molecular beam to define its incident kinetic energy. In this way, we are able to make energy-resolved measurements of reactivity while systematically varying the distribution of energy among the system's energetic degrees of freedom. Computational studies by our collaborators inform and guide our interpretation of the data.

Recent results will be featured and examine the impact of a vibrationally excited reagent molecule's symmetry on surface-induced energy redistribution, the quenching lifetime of a vibrationally excited molecule on a metal surface, the role of surface atom motion on reaction energetics, the ability to use these measurements to benchmark DFT electronic structure calculations, and how isolated surface structural features, including steps and adatoms, modify reaction energetics.

4:20pm **HC+SS-WeA7 Vibration-driven Reaction of CO_2 on Cu Surfaces via Eley-Rideal Type Mechanism***, **Junji Nakamura**, J.M. Quan, T. Kozarashi, T. Mogi, T. Imabayashi, K. Takeyasu, T. Kondo,* University of Tsukuba, Japan

We have long studied the formation of formate ($HCOO_a$) intermediates as an intermediates of methanol synthesis by hydrogenation of CO_2 on Cu surfaces [1-4]. It has been suggested based on the kinetic analysis for the

---

[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

high pressure bulb experiments that the formate formation proceeds via Eley-Rideal type mechanism, in which CO_2 directly reacts with adsorbed hydrogen atom on Cu. In order to clarify the mechanism and dynamics, we carried out CO_2 molecular beam studies with the translational energy of 1.12-1.97 eV and the nozzle temperature of 800-1100 K. It was found that hot CO_2 in the molecular beam reacts directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces at 120–220 K to form formate adspecies ($CO_2 + H_a \rightarrow HCOO_a$). That is, even at the low surface temperatures, formate species is formed rapidly when supplying energy only to CO_2. This indicates that the energy to overcome the reaction barrier comes from the hot CO_2 molecule itself instead of the Cu surface. The vibrational energy of CO_2 was much more effective for the reaction compared to the translational energy; and the reaction rate was independent of the surface temperature. The independence of surface temperature indicates the E-R type mechanism that the CO_2 molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a. If the impinging CO_2 molecule chemisorbs on the Cu surfaces before reacting with H_a, the reaction rate should be dependent on the surface temperature, rather than the kinetic and the internal energies of CO_2. We evaluated the barrier distribution factors (*W*) of so-called Luntz equation by analysis of the reaction probability curves, which shows significant efficacy of the vibrational energy on the reaction of CO_2, which has not been observed before. DFT calculations are consistent with the experimental observations [5]. The direct reaction of CO_2 with adsorbed hydrogen atom can be regarded as the first example of vibration-driven bond formation reactions on surfaces.

References

J. Nakamura, Y. Choi, T. Fujitani, Top. Catal. 22, 277 (2003).

H. Nakano, I. Nakamura, T. Fujitani, and J. Nakamura, J. Phys. Chem. B 105, 1355 (2001).

G.Wang, Y.Morikawa, T.Matsumoto, and J.Nakamura, J. Phys. Chem. B 110, 9 (2006).

J. Quan, T. Kondo, G. Wang, and J. Nakamura, Angew. Chem. Int. Ed. 56, 3496 (2017).

F. Muttaqien, H. Oshima, Y. Hamamoto, K. Inagaki, I. Hamada, Y. Morikawa, Chem. Commun. 53, 9222 (2017).

4:40pm **HC+SS-WeA8 First Principles Reaction Kinetics over Metals, Oxides and Nanoparticles***, **Henrik Grönbeck,*** Chalmers University of Technology, Gothenburg, Sweden **INVITED**

A major challenge in heterogeneous catalysis research is the determination of dominating reaction paths and kinetic bottlenecks. One reason for the challenge is the dynamic character of the kinetics, where the active sites may change with reaction conditions. Nevertheless, it is atomic scale information that allow for catalyst development beyond trial-and-error approaches. Kinetic modeling based on first principles calculations have over the past decade grown into an important tool for investigating the importance of different catalyst phases and reaction paths. In this contribution, I will discuss work where we have used density functional theory in combination with kinetic modeling to investigate catalytic reactions over metals, oxides and nanoparticles. The examples cover different aspects of kinetic modeling including determination of adsorbate entropies, importance of attractive adsorbate-adsorbate interactions and the complexity of many types of active sites.

Complete methane oxidation to carbon dioxide and water is used as one example and we have investigated the reaction over metallic Pd(100) and Pd(111) [1] as well as PdO(101) [2]. The reaction paths are shown to be markedly different on the metallic and the oxidized surfaces. We find that the catalytic activity is highly sensitive to adsorbate-adsorbate interactions which for PdO(101) are attractive owing to electronic pairing effects. This effect is crucial and common for oxide surfaces [3].

Reactions over platinum nanoparticles are investigated using a recently developed scaling relation Monte Carlo technique [4]. Taking CO oxidation as a model reaction, we find that the overall activity is determined by complex kinetic couplings. Effects of particle shape as well as internal and external strain will be discussed [5].

[1] M. Jørgensen, H. Grönbeck, ACS Catalysis, 6, 6730 (2016).

[2] M. Van den Bossche, H. Grönbeck, J. Am. Chem. Soc. 137, 37 (2015).

[3] M. Van den Bossche, H. Grönbeck, J. Phys. Chem. C 120, 8390 (2017).

[4] M. Jørgensen, H. Grönbeck, ACS Catalysis 7, 5054 (2017).

[5] M. Jørgensen, H. Grönbeck, Angew. Chem. Int Ed. (2018).

5:20pm **HC+SS-WeA10 Formation of Pd/Ag Sandwiches, a Stable PdAg Subsurface Alloy, and the Pd Segregation induced by CO and O₂, Studied with STM, Ambient-pressure XPS, and DFT***, **Matthijs van Spronsen,*** Lawrence Berkeley National Laboratory*; K. Duanmu,* UCLA*; R. Madix,* Harvard University*; M.B. Salmeron,* Lawrence Berkeley National Laboratory*; P. Sautet,* UCLA*; C. Friend,* Harvard University

Efficient chemical production requires the use of materials able to selectively catalyze complex chemical reactions. High selectivity can be obtained by using noble metals. To improve activity, while retaining selectivity, small amounts of an active metal can be added. These species can function as active sites for, e.g., O_2 activation.

A promising alloy for selective hydrogenation is AgPd. The challenge using this material as a catalyst is the larger surface free energy of Pd, compared to Ag. This difference leads to Ag enrichment of the surface, hence, more Pd, both costly and scarce, is needed to ensure that Pd is present in the surface.

Here, the stability of Pd was probed in (sub)surface alloys formed by depositing sub-monolayer amounts of Pd on pure Ag single crystals, in order to evaluate the feasibility of using surface alloys as catalysts. These surface alloys would use much less Pd, but depend critically on understanding and control of the alloy composition and stability.

Mild annealing (~400 K) under ultra-high vacuum, leads to extensive migration of Ag and the formation of a Ag capping layer on the Pd. These measurements were based on scanning tunneling microscopy and X-ray photoelectron spectroscopy, supported by modeling (density functional theory). The etching, due to the loss of Ag, and the increase in island height, due to the capping, results in three-layer-high islands, covering both the terraces and the steps of the Ag(111) surface. The absence of significant amounts of Pd in the surface was confirmed by the lack of CO adsorption at 120 K.

The exposure of the Ag/Pd/Ag(111) surface alloy to gas atmospheres, either pure CO or O_2 (0.5 & 1 Torr, respectively), reverses the energetics, thus making Pd resurface. This was concluded from large core-level shifts observed in AP XPS measurements. Due to the proximity of Pd to the surface, the required temperature for Pd to segregate was rather low, in fact, for CO it was detected for 300 K. Resurfacing, and subsequent oxidation, of Pd was much slower, requiring cycling the temperature between 300 and 400 K in the O_2 atmosphere, several times. The difference stems from the fact that O_2 needs to be dissociated before it can form strong bonds to Pd, while CO can adsorb directly to Pd. The initial O_2-dissociation activity of the Ag-capped Pd is expected to be rather small.

To conclude, precise understanding of the stability of active metals with a high surface free energy is required to control the composition of surface alloys and its potential as active/selective catalyst.

Nanometer-scale Science and Technology Division
Room 203A - Session NS+MN+PC+SS-WeA

IoT Session: Bio at the Nanoscale

Moderators: Juraj Topolancik, Roche Sequencing Solutions, Liya Yu, NIST Center for Nanoscale Science and Technology

3:00pm **NS+MN+PC+SS-WeA3 Nanoscale Label-free Imaging of Protein Molecules via Photo-induced Force Microscopy***, D. Nowak,* ***Sung Park,*** Molecular Vista

Nanoscale real space imaging of biological and biomaterial surface is not straightforward even with advances in microscopy techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. For protein molecules, amide I and II bands are readily accessible via tunable quantum cascade laser and provide ways to interrogate the molecule's local chemical environment. PiFM can provide both high resolution spectral imaging at a fixed wavenumber and full PiFM spectrum (analogue to FTIR spectrum) with a spectral resolution of 1 cm^{-1} and spatial resolution of sub-10 nm. Results on collagen molecules, individual icosahedral protein cages, and nanoparticle/protein systems will be presented.

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

3:20pm **NS+MN+PC+SS-WeA4 Evaluating Reaction-diffusion Immunoassays via High-resolution Imaging Techniques***, **Imanda Jayawardena**,* University of Queensland, Australia*; S. Corrie,* Monash University, Australia*; L. Grondahl,* University of Queensland, Australia

Immunodiffusion is a simple assay used for the determination of a target protein concentration in a biological sample using a distance-based measurement. The assay allows the sample containing the antigen of interest to combine with an antiserum in a gel-based substrate leading to the formation of a ring-shaped precipitate ('precipitin ring'), the size of which is proportional to target protein concentration.[1] Using the malarial antigen HRP2 and antisera from immunized rabbits as the model system, for the first time, we are investigating transforming the current immunodiffusion assays into a more rapid and sensitive format.

The traditional assay substrate, agarose, is a severely diffusion limited system. The porosity of the gel is a key determinant of diffusion properties and is an essential parameter required for the study and modification of the assay. However, the scientific data on agarose pore size determination is based on artefact laden microscopy images of agarose hydrogels. Thus, we have performed an in-depth investigation on best imaging techniques for accurate pore size determination. The precipitin ring structure is a band of antigen-antibody precipitate, in significant contrast with the surrounding gel substrate. A brief preliminary investigation has been reported by Fedorov et al. on precipitin ring structure[2], and we have extended this work by applying microscopic imaging techniques.

For imaging hydrogels, high pressure frozen gels were subjected to cryo-SEM[3], and was established as the most accurate technique to study the native structure of the gel. Atomic force microscopy was found to complement cryo-SEM data while CLSM due to its limited resolution was found to be inadequate for the imaging of hydrogels. For imaging the protein-rich precipitin ring structure, high pressure frozen ring sections were subjected to cryo-SEM, however, more meaningful insight on the ring structure was obtained in this instance through CLSM studies.

Herein, we aim to present our work described above on imaging agarose hydrogels for accurate pore size determination and imaging precipitin ring structures associated with immunodiffusion assays.

1. Mancini, G.; Carbonara, A. t.; Heremans, J. *Immunochemistry* **1965**
2. Fedorov, A. A.; Kurochkin, V. E.; Martynov, A. I.; Petrov, R. V. *Journal of Theoretical Biology* **2010**
3. Aston, R.; Sewell, K.; Klein, T.; Lawrie, G.; Grøndahl, L. *European Polymer Journal* **2016**

4:20pm **NS+MN+PC+SS-WeA7 The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High Resolution AFM***, **Uri Sivan**, K. Kuchuk, I. Schlesinger,* Technion - Israel Institute of Technology, Israel **INVITED**

Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

After a short presentation of our home-built microscope, characterized by sub 0.1 Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success in obtaining ultra-high resolution images of DNA and 3d maps of its hydration structure. This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

5:00pm **NS+MN+PC+SS-WeA9 Open-hardware, High-speed Atomic Force Microscopy using Photothermal Off-resonance Tapping***, **Georg Fantner**,* École Polytechnique Fédéral de Lausanne, Switzerland **INVITED**

Self-assembly of protein complexes is at the core of many fundamental biological processes. To reach a comprehensive understanding of the underlying protein self-assembly reactions, high spatial and temporal resolution must be attained. This is complicated by the need to not interfere with the reaction during the measurement. Since self-assemblies are often governed by weak interactions, they are especially difficult to monitor with high-speed atomic force microscopy due to the non-negligible tip-sample interaction forces involved in current methods. Here we develop a high-speed atomic force microscopy technique, photothermal off-resonance tapping (PORT), which is gentle enough to monitor self-assembly reactions driven by weak interactions. Using photothermal actuation on ultra-small HS-AFM cantilevers we perform force-distance curves at two orders of magnitude higher rates than in conventional off-resonance methods. From the time-domain tip sample interaction we extract tip-sample force curves to quantify the *"static"*forces due to the cantilever deflection, and the *"impact"* forces due to the rapid deceleration of the cantilever tip upon impact. Experimental characterization of the tip-sample forces in HS-tapping mode-AFM and PORT revealed that imaging forces in PORT are less than 1/5thof those exerted in conventional HS-AFM.

One of the key enabling factors for PORT is the real time control of the cantilever position using photothermal excitation. This requires low level, control of the feedback architecture and optimized AFM instrumentation. I will discuss the relevant components developed in my laboratory and explain how we share them with the broader scientific community using an open-hardware scheme.

We apply PORT to dissect the self-assembly reaction of SAS-6 proteins, which form a nine-fold radially symmetric ring-containing structure that seeds formation of the centriole organelle present in all eukaryotic cells. Using machine learning algorithms we traced hundreds of molecules over time to extract reaction kinetics from single molecule interactions. These measurements show that 9-fold closed SAS-6 rings are under pre-tension in their natural state. Due to the high temporal and force resolution provided by PORT, we found that, contrary to the current belief, more than one assembly route exists to reach the nine fold symmetry. These observation resets our current thinking about the assembly kinetics of this crucial step in cell replication.

5:40pm **NS+MN+PC+SS-WeA11 Development of Multimodal Chemical Nano-Imaging for *in situ* Investigations of Microbial Systems***, A. Bhattarai, B.T. O'Callahan, P.Z. El Khoury, **Scott Lea**,* Pacific Northwest National Laboratory*; K.-D. Park, E.A. Muller, M.B. Raschke,* University of Colorado Boulder

Existing genomic and biochemical methods cannot directly probe the physical connections involved in microbial metabolic processes over relevant length scales, spanning the nano-meso-micrometer spatial regimes. Determining the location and function of such biomolecules would aid in identifying the mechanisms governing microbial interactions. We are addressing these technical and conceptual gaps by developing a single multimodal chemical imaging platform that can interrogate biomolecules in living systems using three complementary label-free, nanoscale, ultrasensitive chemical imaging techniques:

Infrared scattering scanning near-field optical microscopy (IR *s*-SNOM)

Tip-enhanced Raman nano-spectroscopy (TERS)

Multimodal hyperspectral optical nano-spectroscopy.

We have built and developed these imaging modalities independently prior to integration into a single, multimodal chemical nanoscope. As part of our benchmarking experiments, we performed TERS measurements targeting prototypical systems and constructs and demonstrated <1 nanometer precision in ambient TERS chemical imaging measurements.[1] We also established an overall broader scope of TERS[2] and illustrated that TERS is not restricted to nanoscale chemical imaging, but can also be used to probe different aspects of local fields confined to a few nanometers. Our new setup, equipped with a hyperspectral imager, enables hyperspectral fluorescence, optical absorption, dark-field scattering, Raman scattering, and topographic imaging. Recently, we used this capability to visualize pigments in lipid monolayers and within a single live *T. lutea* cell in solution.[3] For IR *s*-SNOM, we are working on developing an AFM capable of bottom illumination and collection of IR light to support measurements in aqueous environments. The approach would use a piezoelectric scanner mounted ZnSe prism to enable evanescent wave illumination and collection of scattered IR light. We are also benchmarking the IR *s*-SNOM with the TERS and hyperspectral imaging modalities on a number of model biological systems including bacteria, collagen, and cytochromes.

This unique AFM-based instrument could be used to investigate a wide range of biomolecules through their characteristic electronic and vibrational signatures, over the nano-meso-micrometer scales. This platform will not only enable recording chemical images of single microbial cells at the subcellular level, but it will also enable mapping entire microbial communities with chemical selectivity.

1. Bhattarai A and El-Khoury PZ (2017) *Chem Commun* **53**(53): 7310-7313.
2. Bhattarai A *et al*. (2017) *Nano Lett* **17**(11): 7131-7137.
3. Novikova IV *et al*. (2017) *Chem Phys* **498-499**: 25-32.

Surface Science Division
Room 203C - Session SS+AS+EM-WeA
Semiconducting Surfaces

Moderators: Melissa Hines, Cornell University, Ludo Juurlink, Leiden University

2:20pm **SS+AS+EM-WeA1 Functionalizing Semiconductor Surfaces and Interfaces**, ***Stacey Bent,*** Stanford University **INVITED**

Semiconductor surface and interface science serves as the foundation for applications ranging from microelectronics to optoelectronics to bio-sensing. Given the importance of semiconductor surface chemistry in important technologies of today, understanding the fundamental chemistry at a molecular level is key to future advances. This talk will describe studies on the adsorption of organic molecules at semiconductor surfaces, aimed at the ultimate goal of controlling the chemical and electrical properties of these hybrid systems. The presentation will examine model systems of molecular adsorption on the Ge(100)-2×1 surface using a combination of experimental and theoretical methods. The reactivity of different functional groups will be described, with particular focus on reactions of bi- and trifunctional molecules. The results help elucidate the way in which the molecular structure as well as the identity of the reactive moieties affect the product distribution of the molecules upon adsorption. Monolayer surface chemistry is also extended to the formation of covalently-bound organic multilayers through the process of molecular layer deposition (MLD). Results will be presented of our studies to understand MLD mechanisms and bonding. We show that chain termination events during MLD can be counteracted by absorption of precursors into the MLD film, which reintroduces reactive sites that lead to continuation of film growth. We will also describe new MLD chemistries, including photo-initiated MLD that forms new carbon-carbon bonds at the surface.

3:00pm **SS+AS+EM-WeA3 Atomic Structure of UHV-prepared GaP(111)A Surface and its Reactivity Towards Simple Molecules**, ***Denis Potapenko,*** *X. Yang, B.E. Koel,* Princeton University

Effective pyridine-catalyzed photo-reduction of CO_2 to methanol has been demonstrated on p-type GaP(111)A photocathode. Despite the considerable effort there is still no consensus about either the molecular mechanisms of this process or the role of electrode's surface. As a part of larger effort aimed at elucidation of the mechanisms of CO_2 photoreduction we have conducted a UHV study of the atomic-scale structure and reactivity of the single-crystal GaP(111)A surface. Atomic-resolution STM images supported by LEED data show that ion sputtered and annealed surface exhibit both 2 x 2 Ga-vacancy reconstruction and relatively disordered P-trimer formations. The stoichiometric excess of Ga leads to formation of large droplets on the surface. TPD experiments and IR spectroscopy with water and methanol demonstrate dissociative adsorption of these molecules that leads to recombinative desorption around 300 K.

3:20pm **SS+AS+EM-WeA4 Stabilization Mechanism of the Se- or S-treated GaAs(111)B Surface**, ***Shunji Goto,*** The University of Electro-Communications (UEC-Tokyo), Japan; *A. Ohtake,* National Institute for Materials Science (NIMS), Japan; *J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

GaAs surfaces are stabilized by surface treatments with S or Se because of the reduction of the dangling bond density [1,2]. Recently, it has been reported that when the GaAs(111)B-(2 x 2) As trimer surface is treated with Se, the diffraction pattern changes from (2 x 2) to (1 x 1) [3]. The Se-treated GaAs(111)B-(1 x 1) surface was considered to have a simple structure; all As atoms of the ideal (111)B surface are replaced by Se atoms. However, a scanning tunneling microscope (STM) image shows highly disordered array of bright features with a density of 0.25 per (2 x 2) unit [4,5]. This is incompatible with the simple structure model for (1 x 1). Very recently, another structure model has been proposed for the Se-treated surface, where three As atoms on the topmost surface are replaced by Se atoms per (2 x 2) unit. This As / Se terminated model is electronically stable because the so-called electron counting rule is satisfied and the STM simulations for this model reproduces the most of features of STM experiments. In this study, we discuss the structural stability of the As / Se termination model from the viewpoint of the formation energy. We depict a phase diagram as functions of chemical potentials of Se (μ(Se)) and As (μ(As)) using the first-principles calculations within the density functional theory.

Under the As-rich and Se-poor conditions, the (2 x 2) As-trimer surface is the most stable phase. The As / Se terminated surface appears in the phase diagram under more As (Se) poor (rich) conditions, being consistent with the recent experiment [5]. It is noted that the fully-Se-terminated (1 x 1) surface can exist as a stable phase in the limit of Se-rich condition, whereas this surface does not satisfy the electron counting rule and has a metallic surface state attributed to surplus electrons of Se. At the fully-Se-terminated surface, a lone pair forms at each Se site and resultant excess electrons occupy the anti-bonding orbital of the outermost bilayer. As a result, the surface Se atoms hardly leave any dangling bond. We have also found that the S-treated surface is passivated by a similar mechanism.

[1] J. Fan, H. Oigawa and Y. Nannichi, Jpn. J. Appl. Phys. 27 L2125 (1988).

[2] V. N. Bessolov and M. V. Lebedev, Fiz. Tekh. Poluprovodn **46**, 10201 (1998).

[3] D. A. Woolf, Z. Sobiesierski, D. I. Westwood, and R. H. Williams, J. Appl. Phys. **71**, 4908 (1992)

[4] A. Ohtake and Y. Sakuma, Cryst. Growth Des. **17**, 363 (2017).

[5] A. Ohtake, S. Goto, and J. Nakamura, Sci. Rep., **8**, 1220 (2018).

4:20pm **SS+AS+EM-WeA7 Novel Pathways in Reaching Buried Interfaces of Organic/Inorganic Hybrid Systems: A Mechanistic Understanding of Polymer Adsorption on Passivated Metal Oxide Surfaces**, ***Tom Hauffman,*** *S. Pletincx, K. Marcoen, F. Cavezza,* Vrije Universiteit Brussel, Belgium; *L.-L. Fockaert, J.M.C. Mol,* Technical University Delft, Netherlands; *H. Terryn,* Vrije Universiteit Brussel, Belgium

The interface between a metal oxide and its coating is of great importance for the durability and efficiency of the entire organic/inorganic hybrid system. However, the analysis of such solid/solid interfaces is challenging, as they are masked by a µm-thick polymer layer on one side and a thick metal oxide matrix on the other side. The main difficulty will be to investigate buried interfaces non-destructively with conventional surface analysis techniques.[1,2]

In this work, we characterize interfacial interactions of several ultrathin polymeric films with aluminum and zinc oxides by utilizing novel methodologies, leading to the characterization of a realistic model interface. The adsorption mechanisms are established by using XPS for chemical state information and ToF-SIMS for direct molecular information of these ultrathin organic overlayers.

The use of these nanometer thin films opens up the possibility of an in situ characterization of environmental influences such as water ingress. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the adsorption mechanism in the presence of water vapor. Furthermore, ATR-FTIR Kretschmann is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized.[3]

The homogeneity of these interfacial interactions is characterized on the nanoscale using nano-infrared spectroscopy. This novel technique allows to conduct infrared spectroscopy on the nanoscale by using an AFM tip, which probes the expansion of the material due to IR absorbance. This results in a local vibrational spectrum.

This work comprises novel synthesis routes and methodologies, which enable to probe interfacial changes in hybrid systems non-destructively and in situ. As such, coatings systems can be optimized with respect to the bare substrate.

(1) van den Brand, J.; Blajiev, O.; Beentjes, P. C. J.; Terryn, H.; de Wit, J. H. W. Interaction of Anhydride and Carboxylic Acid Compounds with

Aluminum Oxide Surfaces Studied Using Infrared Reflection Absorption Spectroscopy. *Langmuir* **2004**, *20*(15), 6308–6317.

(2) Hinder, S. J.; Lowe, C.; Maxted, J. T.; Watts, J. F. A ToF-SIMS Investigation of a Buried Polymer/polymer Interface Exposed by Ultra-Low-Angle Microtomy. *Surf. Interface Anal.* **2004**, *36*(12), 1575–1581.

(3) Pletincx, S.; Trotochaud, L.; Fockaert, L.-L.; Mol, J. M. C.; Head, A.; Karslıoğlu, O.; Bluhm, H.; Terryn, H.; Hauffman, T. In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.* **2017**, *7*(45123).

4:40pm **SS+AS+EM-WeA8 Surface Modification of Metal Oxide Surfaces with Gas-Phase Propiolic Acid for Dye Sensitization by Click Reaction***, **Chuan He**, A.V. Teplyakov, B. Abraham, M. Konh, Z. Li, L. Gundlach, S. Bai,* University of Delaware*; E. Galoppini, H. Fan, R. Harmer,* Rutgers, the State University of New Jersey

The dye sensitization on metal oxide (ZnO, TiO_2, Fe_2O_3, CuO) surfaces has attracted plenteous attention due to their numerous applications in solar energy conversion, photo-catalysis, sensing, etc. Substantial research efforts focused on designing different dyes and surface nanostructuring. However, the actual chemical attachment schemes still heavily rely on the use of sensitizer molecules functionalized with carboxylic (COOH) or phosphonic ($P(O)(OH)_2$) anchor groups. Despite consequential progress in chemical modification schemes, the very nature of these functional groups may cause very pronounced surface morphology change of the nanomaterials designed because of etching process in liquid phase. In addition, these acidic groups often lead to the formation of multiple binding configurations (such as monodentate or bidentate miixtures) on the surface. To address both issues, we developed a two-step preparation procedure to achieve the morphology preservation of metal oxide surfaces and well-defined covalent binding of the intersurface functionality. The first step requires exposing clean metal oxide nanostructures to a gas-phase prop-2-ynoic acid (propiolic acid) in medium or high vacuum, which results in the formation of a robust and stable surface-bound carboxylate with ethynyl groups available for further modification. For the second step, we applied copper catalyzed click reaction on this preserved surface to covalently bind dye molecules functionalized with azido groups to these pre-functionalized surfaces. For example, a suitable organic dye (9-(4-azidophenyl)-2,5-di-tert-butylperylene (DTBPe-Ph-N_3)) was used to investigate a distinct signature of covalently-bound dye molecules on ZnO nanorods surface. In this study, we have confirmed the morphology preservation and selective covalent attachment of the carboxylic acid onto the metal oxide surface by the combination of measurements including scanning electron microscopy (SEM), infrared, X-ray absorption photoelectron spectroscopy (XPS), solid-state 13C NMR, transient absorption spectroscopy (TA) and density functional theory (DFT) calculations.

5:00pm **SS+AS+EM-WeA9 Solar Energy Storage in the Norbornadiene-quadricyclane System: From Surface Science to In-situ Photochemistry and photospectroelectrochemistry***, M. Schwarz, F. Waidhas, C. Schuschke,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; S. Mohr,* Friedrich-Alexander-Universität Erlangen-Nürnberg*; O. Brummel, T. Döpper, C. Weiss, K. Civale,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Jevric,* Chalmers University of Technology, Gothenburg, Sweden*; J. Bachmann,* Friedrich-Alexander-Universität Erlangen-Nürnberg. Germany*; A. Görling, A. Hirsch,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; K. Moth-Poulsen,* Chalmers University of Technology, Gothenburg, Sweden*; **Jörg Libuda**,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Photochemical isomerization of small organic molecules enables chemical energy storage via a single-photon-single-molecule process. A prototypical example is the conversion of norbornadiene (NBD) to its strained metastable valence isomer quadricyclane (QC), which releases up to 100 kJ/mol upon cycloreversion. This makes the NBD-QC system a solar fuel with an energy density comparable to state-of-the-art batteries.

In order to obtain a better understanding of NBD-based energy storage systems, we studied both the photochemical conversion and the catalytically and electrochemically triggered back-conversion at atomically defined interfaces. We combined vibrational spectroscopy with in-situ photochemistry in ultrahigh vacuum (UHV) and in electrochemical (EC) environments. In UHV, NBD and QC films were grown by physical vapor deposition (PVD) on Pt(111). By infrared refection absorption spectroscopy (IRAS), we observe spontaneous cycloreversion in QC monolayers even at 130 K, while QC multilayers are stable. Adsorbed NBD adopts a η_2:η_1 geometry which involves an agostic C-H-Pt interaction. At 300 K, this species undergoes dehydrogenation by splitting off the agostic H.

In UHV environments, the conversion from NBD to QC can be triggered in-situ by UV light and a co-deposited photosensitizer (PS). In electrochemical environments, back-conversion can be triggered by the electrode. On Pt(111) electrodes, we monitored the back-conversion in-situ by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). The corresponding spectra were analyzed based on simulated spectra from density functional theory (DFT). Using a new photoelectrochemical IRRAS setup (PEC-IRRAS), we monitored the complete storage and release cycle by in-situ vibrational spectroscopy. Selectivities were determined both for the conversion and the back-conversion, showing that the stability of the PS is a critical step in the storage cycle. Much higher reversibility could be obtained using new NBD derivatives which avoid an additional PS.

To better control the energy transfer via the electrode interface, we investigated NBD derivatives anchored via a carboxylic-acid function to atomically defined oxide surfaces. In UHV, dense monolayers of surface-anchored NBD derivatives were prepared by PVD onto Co_3O_4(111) films on Ir(100). The molecules adopt an upright-standing orientation with the NBD units pointing away from the interface. Finally, we explored the behavior of these films in (photo)electrochemical environments.

[1] O. Brummel et al., ChemSusChem 9, 1424 (2016).

[2] U. Bauer at al., Chem. Eur. J. 23, 1613 (2017).

[3] O. Brummel et al., J. Phys. Chem. Lett., 8, 2819 (2017).

5:20pm **SS+AS+EM-WeA10 In-situ Characterization of Photon induced Chemistries in Organotin Clusters with Ambient Pressure XPS***, **J. Trey Diulus**[1], R.T. Frederick,* Oregon State University*; M. Li,* Rutgers, the State University of New Jersey*; D.C. Hutchison, I. Lyubinetsky, L. Árnadóttir, M.R. Olsen,* Oregon State University*; E.L. Garfunkel,* Rutgers, the State University of New Jersey*; M. Nyman,* Oregon State University*; H. Ogasawara,* SLAC National Accelerator Laboratory*; G.S. Herman,* Oregon State University

Solution-based organometallic nanoclusters are unique nanoscale material precursors due to the precise control over their size, shape, and structure. The interaction of photons with these clusters can result in the preferential removal of organic ligands at room temperature. This process leads to a change in solubility, which makes these materials prime candidates for next-generation photoresists for extreme ultraviolet (EUV) nanolithography. In this study, we are investigating the interaction of soft X-ray radiation with organotin based clusters to better understand the transition from organometallic to metal oxide nanoclusters. As a model system we are studying the charge neutral, sodium templated, butyl-tin Keggin (β-$NaSn_{13}$) cluster $[NaO_4(BuSn)_{12}(OH)_3(O)_9(OCH_3)_{12}(Sn(H_2O)_2)]$. For analysis, the β-$NaSn_{13}$ clusters were dissolved in 2-heptanone and spin-coated to form uniform thin films (~20 nm thick). Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to measure the Sn 3d, O 1s, and C 1s core-levels, using photon energies above and below key absorption edges. These measurements allowed us to characterize changes in the both the atomic concentrations and chemical states of β-$NaSn_{13}$ under a range of ambient conditions, including ultrahigh vacuum and multiple partial pressures (between 0.01 to 1 Torr) of oxygen, water, methanol, nitrogen, and hydrogen. Successive C 1s scans were collected during exposure to measure the change in intensity with respect to exposure time, ambient, and photon energy. A significant reduction in the C 1s signal was observed for oxygen ambients, suggesting the oxygen partial pressure was able to increase the rate of butyl group desorption from the β-$NaSn_{13}$ clusters. Furthermore, a photon dose array was collected in each condition to determine whether ambient conditions have an effect on the photon induced chemistries leading to a solubility transition. The dose array was plotted as contrast curves, which indicate that an oxygen ambient significantly lowers the required photon dose relative to UHV. We also found that a water ambient significantly increases the required photon dose compared to an oxygen or UHV ambient. These studies ultimately improve the understanding of photon induced chemistries in the β-$NaSn_{13}$ based thin films and provide mechanistic insights for the formation of tin oxide nanomaterials at surfaces.

5:40pm **SS+AS+EM-WeA11 Integrated Photonics Driven Electron Emission from LaB_6 Nanoparticles***, **Fatemeh Rezaeifar**, R. Kapadia,* University of Southern California

In this report, we demonstrate the novel approach of integrated photonics waveguide driven electron emission from Lanthanum hexaboride (LaB_6)

---

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

nanoparticles drop-casted over the surface of an optical waveguide. We use integrated waveguide under LaB_6 electron emitter as a mean to transport photons and evanescently couple them to emitter. This evanescent coupling occurs through longer interaction length and photons can be absorbed efficiently compared to free space laser illumination from top on a metallic emitter. Furthermore, nanoparticles with the average diameter of 4 nm are at the order of electron mean free path and electron emission occurs with fewer scattering compared to electron emission from conventional bulky metallic emitters. As such, in our proposed device, the higher optical absorption along with fewer scattering inside nanoparticles enable us with larger quantum efficiency electron emitters beyond the available photon driven emitters.

We experimentally studied the photon driven electron emission characteristics obtained by coupling of CW laser (wavelength = 405 nm) to LaB_6 nanoparticle emitters drop-casted on top surface of the silicon nitride (Si_3N_4) integrated waveguide with height of 5 µm and width of 50 µm. Optical V-groove was fabricated for coupling 405 nm laser from 200 µm optical fiber in to Si_3N_4 waveguide. The work function of the LaB_6 is only 2.69 eV and it requires very small E-field to collect the photon driven emitted electrons. We observed photocurrent at E-field as small as 0.3 V/µm while the dark current detection from LaB_6 nanoparticles begins at higher E-field, 3.5 V/µm. In addition, we present the photocurrent dependency on the laser power. At small E-field in which no tunneling is possible, we observed a linear relation between the photocurrent and laser power indicating single photon ability for this emission process. This matches to the expected slope of 1 for single photon absorption process, given that the work function of LaB_6 is only 2.69 eV, and our photon energy at 405 nm is 3.1 eV. Finally, we present the comparative results for the emission properties from LaB_6 nanoparticles illuminated with free space laser to evaluate the performance of the proposed integrated photonics driven emitters. While free space illuminated method results in emission current as small as 1 pA with 390 mW of laser power, the integrated photonics driven emitter emits above 50 pA with much smaller laser power transporting inside the optical waveguide, 100 µW. As such, we conclude integrated photonics driven emitter as a potential solution for increasing the quantum efficiency of the future electron emitters.

6:00pm **SS+AS+EM-WeA12 Photon Stimulated Desorption and Diffusion of CO on TiO_2(110)**, ***Nikolay Petrik***, *R. Mu, A. Dahal, Z.-T. Wang, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel,* Pacific Northwest National Laboratory

Thermal diffusion of CO adsorbed on rutile TiO_2(110) was studied in the 20 - 110 K range using photon-stimulated desorption (PSD), temperature programmed desorption (TPD) and scanning tunneling microscopy. During UV irradiation, CO desorbs from certain photoactive sites (e.g. oxygen vacancies). This phenomenon was exploited to study CO thermal diffusion in three steps: first empty these sites during a first irradiation cycle, then replenish them with CO during annealing, and finally probe the active site occupancy in the second PSD cycle. The PSD and TPD experiments show that the CO diffusion rate correlates with the CO adsorption energy – stronger binding corresponds to slower diffusion. Increasing the CO coverage or hydroxylation of the surface decreases the CO binding and increases the CO diffusion rate. Relative to the reduced surface, the CO adsorption energy increases and the diffusion decreases on the oxidized surface. The CO diffusion kinetics can be modeled satisfactorily as an Arrhenius process with a “normal” prefactor (i.e. $\nu = 10^{12}\ s^{-1}$) and a Gaussian distribution of activation energies where the peak of the distribution is ~0.28 eV and the full width at half maximum (FWHM) is ~0.1 eV at the lowest coverages. The observations are consistent with a significant electrostatic component of the CO binding energy on the TiO_2(110) surface which is affected by changes in the surface dipole and dipole-dipole interactions.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+MN+NS+SS-ThM
Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni_xPd_{1-x} (111) Substrates***, **Chao Zhou**, X. Liang, G.S. Hutchings, Z. Fishman, J.-H. Jhang, S. Hu, S. Ismail-Beigi, U.D. Schwarz, E.I. Altman,* Yale University

The discrete lattice constants and distinct chemical properties of different transition metal substrates hamper the systematic study of how the substrates can influence two-dimensional (2D) materials growth. The recent report of single-crystal epitaxial Ni-Pd alloy films with continuously tunable lattice constants open the possibilities to tackle this issue. Two-dimensional silica and transition-metal-doped silicate films prepared on metal substrates can be 2D analogues of porous bulk zeolites. In this research, 2D silica and Ni-silicate films were prepared on Ni_xPd_{1-x} (111) substrates under different growth conditions. After annealing in 2×10^{-6} Torr oxygen, Ni from the alloy substrates incorporates into the silica structure to form a crystalline 2D Ni-silicate structure, while an amorphous 2D silica bilayer can be observed after being annealed in 4×10^{-8} Torr oxygen. Density functional theory (DFT) was employed to model various silica and silicate phases on Ni_xPd_{1-x} (111) substrates. The results show that the 2D Ni-silicate films are thermodynamically stable on the substrates when the oxygen chemical potential is in the oxygen-rich range. In oxygen-deficient environments, 2D silica tends to form a stable Ni-free phase. With continuous control over the composition of NiPd alloy films, the surface strain applied on the Ni-silicate films through the lattice mismatch between the substrate and overlayer could also be continuously tuned. Only single-domain commensurate crystalline 2D Ni-silicate can be observed in zero or low-strain systems, while a second incommensurate crystalline domain which is rotated by 30° with respect to the commensurate domain can be observed when the lattice mismatch is over 1.85%.

8:40am **2D+EM+MI+MN+NS+SS-ThM3 Topological Materials***, **Hsin Lin**,* Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi_2Se_3 series, the ternary half-Heusler compounds, $TlBiSe_2$ family, Li_2AgSb-class, and $GeBi_2Te_4$ family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, $SrSi_2$, $(Mo,W)Te_2$, Ta_3S_2, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition***, **Michael Valentin**,* Army Research Laboratory*; A. Guan, A.E. Nguyen, I. Lu, C.S. Merida, M.J. Gomez,* University of California, Riverside*; R.A. Burke, M. Dubey,* Army Research Laboratory*; L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS_2), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS_2 is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging***, M.A. Susner,* Air Force Research Laboratory*; M.A. McGuire, **Petro Maksymovych**,* Oak Ridge National Laboratory

Recently, the family of transition metal thiophosphates –exhibiting ferroelecric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown.

Here we present the first atomically resolved imaging of $CuScP_2S_6$ s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc^{3+} within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with $CuInP_2S_6$ – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Susner Michael A., Chyasnavichyus Marius, McGuire Michael A., Ganesh Panchapakesan, and Maksymovych Petro, Advanced Materials **29**, 1602852 (2017).

[2] S. M. Neumayer, E. A. Eliseev, M. A. Susner, A. Tselev, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, ArXiv:1803.08142 [Cond-Mat] (2018).

11:00am **2D+EM+MI+MN+NS+SS-ThM10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators***, **Paul Dietrich**, M. Wietstruk, T.U. Kampen, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

Modern ARPES analyzers provide a high degree of parallelization in data acquisition, recording hundreds of energy and angle channels simultaneously. Additionally, integrated deflectors enable users to perform angle scanning perpendicular to the analyzer's entrance slit to record (k_x, k_y, E) data sets without sample rotation. However, the design of conventional analyzers implies a limited acceptance angle and corresponding accessible momentum space volume. Due to the trade-off between acceptance angle and angle resolution multiple changes in sample position and lens modes are necessary during a typical high resolution ARPES experiment. The new KREIOS 150 Energy Analyzer uses an extractor zoom lens design to overcome these limitations.

This new lens provides a full solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis.

The capabilities of this instrument were tested at the UE 56/2 at the Bessy II synchrotron in Berlin. Specification tests show excellent angle and lateral resolution as well as small spot capability down to 2µm FOV. Subsequently real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on $NbSe_2$ excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

Acknowledgements: We thank Yu. Dedkov (University of Shanghai, China) and M. Fonin (University Konstanz) for providing beamtime and samples for the measurements with KREIOS 150 at BESSY II.

11:20am **2D+EM+MI+MN+NS+SS-ThM11 Carbon Nanomembranes with Sub-nanometer Channels: 2D Materials for Water Purification with High Selectivity and Highest Permeance***, Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X.H. Zhang, A. Beyer, S. Koch, D. Anselmetti,* ***Armin Gölzhäuser,*** Bielefeld University, Germany

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of ~10^{18}m^{-2}. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of ~1.1×10^{-4} mol·m^{-2}·s^{-1}·Pa^{-1}. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels.Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules·s^{-1}·Pa^{-1}.We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

[1] A. Turchanin and A. Gölzhäuser: Carbon Nanomembranes, *Adv. Mater*. **2016,**28, 6075.

[2] Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, A. Gölzhäuser, *ACS Nano*, in press.

11:40am **2D+EM+MI+MN+NS+SS-ThM12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy***,* ***Iwao Matsuda,*** University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu_2Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation. I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

[1] B. Feng, IM *et al*.,Phys. Rev. Lett., **118**, 096401 (2017) .

[2] B. Feng, IM *et al*.,Adv. Mater. **30**, 1704025 (2018) .

[3] B. Feng, IM *et al*.,Nature Comm., **8**, 1007 (2017) .

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-ThM

In-situ Analysis of Heterogeneously Catalyzed Reactions

Moderator: Sharani Roy, University of Tennessee Knoxville

8:00am **HC+SS-ThM1 Structural Characterization of ZnO on Cu(111) by using STM and XPS: Role of Cu-ZnO Interface in Methanol Synthesis***,* ***Mausumi Mahapatra,*** *J.A. Rodriguez,* Brookhaven National Laboratory

The ZnO–copper interface plays an important role in the synthesis of methanol from the hydrogenation of (CO_2+ $4H_2$--> CH_3OH + $2H_2O$). The deposition of nanoparticles of ZnO on Cu(111), θ_{oxi} < 0.3 monolayer, create a stable and highly active interface between ZnO and Cu. The ZnO-copper catalysts may be prepared by two different methods: 1) Zn vapor deposited on Cu(111) at ~600 K in an oxygen ambient (reactive vapor deposition), 2) Zn vapor deposited on Cu(111) at 300 K following by heating the surface with oxygen to 600 K (oxidation of surface alloy). The reactivity and stability of the catalysts prepared by the above two methods were tested under CO_2 hydrogenation reaction conditions in a reactor and by using AP-XPS: 1) The ZnO-copper catalyst prepared by method 1 was stable whereas that prepared by method 2 was not stable at the elevated temperatures (500–600 K) used for the CO_2 hydrogenation. The temperature dependent growth and the structural characterization of the ZnO/Cu(111) catalyst, θ_{oxi} < 0.3 monolayer was explored by using STM. Our results show that the size and shape of the ZnO nanoparticles are dependent on the growth temperature. The ZnO/Cu(111) surface prepared by reactive vapor deposition at 450-600 K results in large ZnO triangular islands. However the surface oxidation of a Zn/Cu(111) alloy resulted in very small ZnO clusters.

8:20am **HC+SS-ThM2 Dissociative Adsorption of CO_2 on Cu-surfaces***,* ***Benjamin Hagman,*** Lund University, Sweden*; A. Posada-Borbón, A. Schaefer,* Chalmers University of Technology, Gothenburg, Sweden*; C. Zhang,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; N.M. Martin,* Chalmers University of Technology, Gothenburg, Sweden*; E. Lundgren,* Lund University, Sweden*; H. Grönbeck,* Chalmers University of Technology, Gothenburg, Sweden*; J. Gustafson,* Lund University, Sweden

Due to the urgent problem of global warming, there is a need to reduce the release of the greenhouse gas CO_2 into the atmosphere. A potential approach to limit the CO_2 release is to convert it into useful chemical products, such as methanol [1]. However, the recycling of CO_2 is a challenging task as the molecule is rather inert, which makes it difficult to activate for reduction and subsequent hydrogeneration. The most used metal for this activation is Cu, and a fundamental understanding of how CO_2 interacts with Cu surfaces would promote the development of new catalysts for the reduction of CO_2 [2].

We have studied the CO_2 interaction with both Cu(100) and stepped Cu(911) surfaces at elevated CO_2 pressures using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS gives us the ability to probe the changes of the surface during the chemical reaction. In our case, we see that CO_2 chemisorbs on the surface and dissociates to O and CO, of which CO desorb, while the atomic oxygen remains on the surface.

For the Cu(100) surface, we observe that the rate of oxygen uptake from CO_2 dissociation is constant until the atomic oxygen coverage approaches 0.25 ML, where the rate decreases. After 0.25 ML the rate remains constant until a saturation appears as the oxygen coverage approaches 0.5 ML. Density Functional Theory (DFT) calculations indicate that CO_2 can adsorb and dissociate on both the terraces and steps on Cu(100), however, the dissociation is expected to take place mainly on the step as the barrier for the dissociation is lower at such sites. The atomic oxygen, from the dissociation at the step, is expected to diffuse away from the step to the terrace, leaving the number of active sites constant, and explaining the constant oxygen uptake rate. Both the experiment and DFT calculations indicate that the atomic oxygen from the dissociation of CO_2 poisons the adsorption and dissociation of CO_2 at an oxygen coverage above 0.25 ML, however, we believe that the step can remain active after 0.25 ML.

To confirm the role of the steps on Cu(100), we have also studied the interaction of CO_2 and Cu(911). We observe the CO_2 adsorption is significantly facilitated by the presence of the steps on the Cu(911) surface as compared to the flat Cu(100). The effect of the facilitated CO_2 adsorption on the subsequent dissociation will be discussed.

References:

[1] W. Wang, et al., Chem. Soc. Rev., **40** (2011), pp. 3703-3727

[2] M. D. Porosoff, et al., Energy Environ. Sci., **9** (2016), pp. 62-73.

8:40am **HC+SS-ThM3 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) Surface Under Ambient Pressure Conditions***, C.M. Kruppe,* ***Michael Trenary,*** University of Illinois at Chicago

Copper catalysts are used in the water gas shift reaction to convert mixtures of carbon monoxide and water to hydrogen and carbon dioxide. Conversely, the reverse water gas shift reaction utilizes carbon dioxide as a resource. Related to the reverse water gas shift reaction is the synthesis of methanol from carbon dioxide and hydrogen. The mechanisms of these reactions involve several possible surface intermediates, each of which should be identifiable by their vibrational spectra. We have used reflection absorption infrared spectroscopy (RAIRS) to study these reactions under ambient pressures in the range of 0.1 to 150 Torr. In the presence of 150 Torr of carbon dioxide, a peak is observed at 1294 cm^{-1}, which is assigned to the symmetric stretch of an adsorbed CO_2 molecule that is bent through its interaction with the surface. Upon addition of 150 Torr of $H_2(g)$ at 300 K, the 1294 cm^{-1} peak of CO_2 is greatly diminished, while new peaks appear due to gas phase water. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. When the Cu(111) surface is annealed to higher temperatures, numerous changes occur in the spectra revealing the formation of a series of surface intermediates containing C–H bonds, including methoxy, OCH_3. The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be easily detected with RAIRS.

9:00am **HC+SS-ThM4 Oxide Formation on Ir(100) Studied by in-Situ Surface X-ray-Diffraction***, **Stefano Albertin**, U. Hejral,* Lund University, Sweden*; R. Felici,* SPIN-CNR, Italy*; R. Martin,* University of Florida*; M. Jankowski,* ESRF, France*; J.F. Weaver,* University of Florida*; E. Lundgren,* Lund University, Sweden

Methane (CH_4) conversion into higher added value hydrocarbons is done through a number of complex catalytic steps, and has been studied for many years [1]. The initial and often rate limiting step in the reaction is the dissociation of the molecule on the metal catalyst surface. Because alkane C–H bonds are among the least reactive known, no process for direct conversion of CH_4 into methanol (CH_3OH) has so far been developed.

IrO_2(1 10) surface grown on Ir(100) has shown facile dissociation of CH_4 at liquid nitrogen temperatures [2], as well as oxidizing H_2 to -OH [3]: two steps that could have importance for the development of a new direct methane-to-methanol catalysts.

In this contribution we will present recent results from in-situ Surface X-ray Diffraction (SXRD) recorded at beamline ID03 at the ESRF from the oxidation of a Ir(100) surface. We find that the Ir(100) surface oxidizes into a bulk oxide at a temperature of 775 K and a pressure of 5 mbar of O_2 similar to what observed in [2], forming a predominantly rutile IrO_2(110) oriented surface. Our study also demonstrates that lowering the partial O_2 pressure or the temperature results in the formation of a number of different Ir sub-oxides similar to the ones found for Ir(111) [4], and the structures formed will be discussed in this contribution.

[1] D. M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, Eds. *Methane Conversion, Vol. 36 of Studies in Surface*

Science and Catalysis (Elsevier, Amsterdam, 1988).

[2] Z. Liang, T. Li, M. Kim, A. Asthagiri, and J. F. Weaver, Science **356** (2017) 299.

[3] Li, T., Kim, M., Liang, Z. et al. Top Catal (2018) 61: 397

[4] Y. B. He, A. Stierle, W. X. Li, A. Farkas,N. Kasper, and H. Over, J. Phys. Chem. C **112** (2008) 11946.

9:20am **HC+SS-ThM5 Dynamic Nanocatalysts: Environmental Effects***, **Beatriz Roldan Cuenya**,* Fritz-Haber Institute of the Max Planck Society **INVITED**

In order to comprehend the catalytic performance of metal nanostructures, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanocatalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. Furthermore, deactivation phenomena taking place under reaction conditions can only be understood, and ultimately prevented, if sufficient information is available on the catalyst morphology, structure, chemical state, and surface composition while at work.

I will first describe novel approaches for the synthesis of size- and shape-controlled nanoparticles and nanostructured metallic films (e.g. Au, Cu, Ag, Zn, CuZn, CuCo, CuNi, AgSn, NiGa) and their functionalization/activation based on plasma treatments. Subsequently, I will illustrate how to follow the evolution of their morphology and surface composition under different gaseous and liquid chemical environments in the course of a catalytic reaction. This will be implemented using a synergistic combination of *in situ* and *operando* microscopy (EC-AFM, STM, TEM) and spectroscopy (XAFS, AP-XPS) methods. It will be highlighted that for structure-sensitive reactions, catalytic activity, selectivity, and stability can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas- and liquid-phase oxidation of 2-propanol and the gas-phase hydrogenation and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the size, shape, composition, chemical state, surface defects and roughness of the catalysts in the activity and selectivity of the former reactions.

11:00am **HC+SS-ThM10 Atomic Layer Deposition (ALD) Synthesis of Au/TiO_2/SBA-15 Catalysts***, W. Ke, X. Qin, **Francisco Zaera**,* University of California, Riverside

Au/Titania catalysts have received much attention in recent years because of their ability to promote photocatalytic water splitting as well as selective low-temperature oxidation reactions. The uniqueness of these catalysts is ascribed to both the nanometer-size of the gold nanoparticles and the reducibility of the titania support. Here we report results from studies on the use of ALD to control the titania film thickness, to tune its degree of reducibility and explore the role of that reducibility in catalysis. SBA-15, a mesoporous solid with well-defined pore structure, was used as the base material in order to be better able to characterize the deposited titania films. Surface reducibility was tested as a function of film thickness by CO infrared-absorption spectroscopy titrations and by EPR, and the catalytic performance via kinetic measurements for CO oxidation. Unique trends were observed at intermediate (2-4 ALD cycles) film thicknesses.

11:20am **HC+SS-ThM11 Enhanced Stability of Pt/Cu Single-Atom Alloy Catalysts: In Situ Characterization of the Pt/Cu(111) Surface in an Ambient Pressure of CO***, **Juan Pablo Simonovis Santamaria**,* Brookhaven National Laboratory

Research in catalysis has steered towards the design and synthesis of more efficient catalysts that can yield better quality products at lower costs. In this regard, bimetallic alloys where the active metal is mono-atomically dispersed have shown unique activity, selectivity and stability compared to their monometallic counterparts. These so called single atom alloys (SAA) are of interest since small amounts of active metals can be used reducing catalysts cost. However, the chemical interactions between active site and reacting molecules are still poorly understood, thus careful characterization of these moieties under reaction conditions is needed to elucidate fundamental reaction steps that can clarify the role of the active site during the catalytic process.

In this study, we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) performed at the 23-ID-2 (IOS) beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory to compare the stability of Pt/Cu(111) SAA in ultrahigh vacuum (UHV) and ambient pressure conditions, particularly how its surface structure and composition can be influenced by the presence of a reactant gas such as CO. Because of the surface and chemical sensitivities of AP-XPS, we can directly probe the Pt atoms to clearly identify surface/subsurface layers of the metal and monitor its evolution under different experimental conditions.

Our study showed that the Pt (0.05 ML)/ Cu(111) SAA is thermally unstable above 400 K under UHV conditions, since higher temperatures cause Pt on the surface to migrate to the subsurface and, eventually, to the bulk. This metal diffusion into the subsurface could lead to the deactivation of a potential catalyst. However, under ambient pressures of CO, the surface and subsurface Pt are thermally stable up to 500 K, resisting diffusion into the bulk. In fact, thermal treatment in CO of a sample that was previously heated under UHV conditions lead to the recovery of Pt that had diffused to the subsurface, suggesting that, within 300-500 K the diffusion process is reversible to some extent. However, this thermal stability as well as surface recovery in CO comes at the expense of slightly enhanced CO−Pt interactions likely caused by the presence of neighboring subsurface Pt resulting from the thermal-induced restructuring of the subsurface layer. Whether the post-heated surface still resists the poisoning effects of CO remains to be seen, but these results demonstrate the importance of studying not only the changes in the surface of a catalyst under reaction conditions but also the near-surface region, which may also influence the reactivity of the catalyst.

11:40am **HC+SS-ThM12 Multiscale Modelling of Metal Oxide Interfaces and Nanoparticles***, **Kersti Hermansson**, P. Mitev, J. Kullgren, P. Broqvist,* Dept of Chemistry-Ångström, Uppsala University, Sweden **INVITED**

Redox-active metal oxide surfaces and interfaces – such as electrodes, catalysts, and sensors – play crucial roles in our society and in the development of new materials and greener technologies. In the scientific literature, a full arsenal of experimental methods are being used to help characterize such interfaces. At the same time, the number of theoretical studies in the literature steadily increases, providing mechanistic information at a detail that is hard to beat by experiment. *Are such theoretical results accurate enough*?

I will describe some of our efforts to develop multiscale modelling protocols for metal oxide surfaces and nanoparticles (e.g. of CeO_2, ZnO and MgO). We combine a range of theoretical methods including ***DFT, tight-binding-DFT*** [1]***, and reactive force-field models*** A key question is whether it is really possible to model redox-active metal oxides *without including the electrons*?

The O_2 chemistry of reducible oxides is rich and famous and I will therefore also discuss various aspects of how adsorbed oxygen on nanoparticles and clusters can stabilize in the form ***superoxide ions*** (O_2^-) and the implications that this may have on their reactivities. Microkinetic modelling results to mimic experimental TPD spectra will be presented as well as mechanistic detail that is currently only possible to obtain from modelling.

The H_2O molecule deserves special attention as ***hydroxylation/hydration*** changes the properties and reactivities of metal oxides, often with far-reaching consequences. We recently studied a thick water film on a ZnO(10-10) surface using MD simulations from a neural-network-generated potential landscape of DFT quality combined with anharmonic vibrational frequency calculations.[2] and were able to relate H-bond structure and frequencies in a meaningful way. In an attempt to reach a step further in terms of understanding found that a ***parabola-like* '*OH frequency vs. in-situ electric field*' *relation*** holds for both intact and dissociated water molecules on ionic surfaces [3], and for both thin and thick films (unpublished).

I will also inform about the European Materials Modelling Council (https://emmc.info/), which aims to promote the use of materials modelling in –not least– industry.

References:

[1] J. Kullgren et al., *J. Phys. Chem. C* 121, 4593−4607 (**2017**).

[2] V.Quaranta et al., *J. Chem. Phys*. 148, 241720 (**2018**).

[3] G. G. Kebede et al., *Phys.Chem.Chem.Phys.* 20, 12678 (**2018**)

Surface Science Division
Room 203C - Session SS+EM+NS-ThM

Defects in and Functionalization of 2D Materials

Moderators: Lars Grabow, University of Houston, Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EM+NS-ThM1 Holes, Pinning Sites and Metallic Wires in Monolayers of 2D Materials***, **Thomas Michely,*** University of Cologne, Germany **INVITED**

The moiré formed by a monolayer of hexagonal boron nitride with Ir(111) provides through a chemisorbed valley region within a physisorbed mesa a unique site for its functionalization. Through gentle ion irradiation and mild annealing a regular array of vacancy clusters is created with the clusters positioned at the valleys where their edges bind to the substrates. Such a nanomesh with a regular array of holes with sizes below 1 nm holds promise for filter applications. Through vapor phase deposition of a variety of materials (e.g. Au or C) arrays of clusters with of tunable size and high thermal stability are formed at valley regions. Compared to the graphene moiré the templating effect of the hexagonal boron nitride moiré is superior due to the uniqueness of the valley pinning site in the unit cell.

Monolayers of hexagonal boron nitride or graphene are also excellent substrates for the on-surface synthesis of new compounds ranging from metal-organic nanowires to transition metal disulfides created by reactive molecular beam epitaxy with elemental sulfur. This synthesis method provides clean, well-decoupled layers with only well-defined defects.

The most exciting defects we observed so far are two types of mirror twin boundaries in MoS_2 islands. In these boundaries we observe for the first time spin-charge separation in real space making use of the unique local spectroscopic capabilities of low temperature STM and STS to identify the position and energy of quantum mechanical states in a one dimensional box. We critically discuss these results in the light of previous related research.

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Moritz Will, Phil Valerius, Charlotte Herbig, Carsten Speckmann, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielić, Marko Kralj, Vasile Caciuc and Nicolae Atodiresei as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.

8:40am **SS+EM+NS-ThM3 CO Chemisorption at Pristine, Doped and Defect Sites on Graphene/Ni(111)*, Mario Rocca,*** *G. Carraro,* University of Genova, Italy*; M. Smerieri, L. Savio,* IMEM-CNR, UOS Genova, Italy*; E. Celasco, L. Vattuone,* University of Genova, Italy

Due to its electrical properties graphene (G) has been successfully used as a sensing element for the detection of different gases reaching ppm sensitivities which are ascribed to the doping induced by adsorption. The sensitivity depends indeed critically on the chemical nature of the gas and is lower for CO than for other poisoning species. The nature of the active sites is, however, still unclear. If it were due to physisorption, the values of the adsorption energy cannot explain the need for high temperature re-generation of the sensing element. Chemisorption must thus be involved, either at defects or by doping, determining the magnitude of the heat of adsorption and consequently the sensitivity and the range of temperatures at which the sensor can operate. In order to clarify these issues we investigated experimentally adsorption of CO on G supported on polycrystalline Cu and Ni(111) by HREELS and XPS.

No adsorbed CO was found at RT while at 100 K chemisorbed CO forms on G supported on Ni(111). G on Cu is on the contrary inert. This result indicates that the nature of the substrate plays an essential role in the adsorption process. The heat of adsorption q is estimated to be about 0.58 eV/molecule at low coverage, so that an equilibrium coverage of 0.1 ML is expected at RT under a CO partial pressure of only 10 mbar. We identify top-bridge graphene as the most reactive configuration.

Doping G/Ni(111) by N_2^+ ion bombardment allows for the formation of a second, more strongly bound moiety, characterized by a CO stretch frequency of 236 meV and by an initial heat of adsorption (0.85 eV/molecule). The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO.

Finally in presence of isolated defects, created by low energy Ne^+ ions bombardment on single layer graphene supported on different substrates (polycrystalline Cu and Ni(111)), no CO adsorption occurs for defected G/Cu, while HREELS peaks form promptly for G/Ni(111). Two moieties, desorbing just above 350 K, are present under vacuum conditions after exposure at RT. The CO stretch frequencies and the ratio of their intensities indicate that they are due to chemisorbed CO at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy indicates that in such regions detachment of the G layer from the substrate occurs.

Amending of vacancies occurs for subsequent exposures, as demonstrated by the reduction of the adsorbed coverage in subsequent CO doses followed by annealing at 380 K, indicating that a Bouduard-like reaction takes place under the graphene cover.

9:00am **SS+EM+NS-ThM4 Geometry of Cu Islands Buried Beneath the Surface of Graphite***, A. Lii-Rosales,* Ames Laboratory and Iowa State University*; S. Julien,* Northeastern University*; Y. Han, J.W. Evans,* Ames Laboratory and Iowa State University*; K.-T. Wan,* Northeastern University*;* ***Patricia A. Thiel,*** Ames Laboratory and Iowa State University

Deposition of Cu on a sputtered graphite surface, in ultrahigh vacuum, can be manipulated to produce buried islands of metallic, multilayer Cu. The Cu islands are covered by a graphitic layer consisting of several graphene sheets. This layer drapes like a tarpaulin over the Cu islands. We have observed flat-topped islands as tall as 40 nm and as wide as 600 nm. One of the most striking features of island geometry is the fact that the slope of the tarpaulin at the sides of the islands is invariant over a wide range of island volumes. The variation of the ratio of island diameter to height as a function of island volume is far less regular in the experimental data, suggesting that kinetic limitations may play a role in determining this parameter. To investigate the physical forces responsible for the island geometries, we develop a model for island shape that incorporates the distortion energy of graphene, adhesion of Cu with graphitic surfaces, adhesion of graphene with graphite, and other parameters. The energy parameters involving Cu surfaces and Cu-carbon interfaces are derived from DFT calculations. The values and trends predicted by the model are discussed and compared with experiment. In particular, the model indicates that the slope of the island sides should be invariant, consistent with experiment.

9:20am **SS+EM+NS-ThM5 Intercalation of O_2 and CO between Graphene and Ru(0001) and the Role of Defects*, Jory Yarmoff*,** *T. Li,* University of California, Riverside

Graphene (Gr) is a fascinating 2D material that is being widely being considered for applications in electronic devices due to its unique electronic and materials properties. Also, because of its high thermal stability and inertness, it is a promising candidate for use as a protection layer for metal substrates. Here, graphene films grown on Ru(0001) are exposed to O_2 and ^{13}CO and investigated with helium low energy ion scattering (LEIS). LEIS spectra collected at different scattering angles can distinguish between adsorbed and intercalated molecules. It is found that O_2 and CO do not adsorb to the graphene surface but instead intercalate between Gr and the substrate. It is shown that a much lower annealing temperature is needed to remove intercalated oxygen than chemisorbed oxygen on bare Ru. During the thermal desorption, some of the graphene is etched away via chemical reaction forming gaseous CO or CO_2. In addition, carbon vacancy defects are produced in the Gr films via 50 eV Ar^+ bombardment. Isolated single carbon vacancy defects enable molecular adsorption at the defect sites and ease the overall intercalation of oxygen. The defects also improve the thermal etching efficiency of Gr by intercalated oxygen. When the defects are large enough to consist of open areas of bare substrate, oxygen dissociatively chemisorbs to Ru. Intercalated ^{13}CO molecules sit upright with the O end on top, as on clean Ru. The CO molecules tilt, however, when the temperature is raised. This is likely due to increased vibrational amplitudes combined with the confining effect of the Gr film.

9:40am **SS+EM+NS-ThM6 Organic-2D Transition Metal Dichalcogenide van der Waals Heterostructures*, Yu Li Huang,*** Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; Z. Song,* National University of Singapore*; D. Chi,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; A.T.S. Wee,* National University of Singapore

The recent emergence of two-dimensional transition metal dichalcogenides (2D TMDs) has led to a rapid burgeoning of the field due to their novel electronic and optical properties with potential electronics/photonics applications. Organic materials, on the other hand, have exhibited great success in the field of flexible electronics, with an extensive number of available molecules with tunable properties. Marrying the fields of organics and 2D TMDs will bring benefits that are not present in either material alone, enabling even better, multifunctional flexible devices. In parallel, the integration of 2D TMDs with selected organics is also a promising and controllable approach to modulate the properties of the TMDs without structural damage, thereby optimizing or even enhancing their desired properties for specific device applications. Central to the realization of all those applications is a fundamental understanding of the organic-2D TMD interface.^{1}

Here, we will present our recent studies on hybrid organic/2D TMD heterostructures.$^{2-4}$ With combined experiments and theoretical modeling, the interfacial interactions between the organic layers and the TMDs as well as the energy level alignment at the interface are explored. The comprehensive understanding of the underlying physical mechanisms that govern the properties of organic-2D TMD interfaces at the atomic scale is of fundamental importance for developing this technique further for device applications.

References:

1. Y. L. Huang, Y. J. Zheng, Z. Song, D. Chi, A. T. S .Wee, S. Y. Quek, *Chem. Soc. Rev.*, 2018, DOI: 10.1039/C8CS00159F (online).

2. Z. Song, Q. Wang, M.-Y. Li, L.-J. Li, Y. J. Zheng, Z. Wang, T. Lin, D. Chi, Z. Ding, Y. L. Huang,A. T. S. Wee, *Phys. Rev. B*, 97, 134102, 2018.

3. Z. Song, T. Schultz, Z. Ding, B. Lei, C. Han, P. Amsalem, T. Lin, D. Chi, S. L. Wong, Y. J. Zheng, M. Y. Li, L. J. Li, W. Chen, N. Koch, Y. L. Huang and A. T. S. Wee, *ACS Nano*, 2017, **11**, 9128-9135.

4. Y. J. Zheng, Y. L. Huang, Y. Chenp, W. Zhao, G. Eda, C. D. Spataru, W. Zhang, Y.-H. Chang, L.-J. Li, D. Chi, S. Y. Quek and A. T. S. Wee, *ACS Nano*, 2016, **10**, 2476-2484.

11:00am **SS+EM+NS-ThM10 Influence of Surface Functionalization on Surface Topography and Growth of Metal Oxide Structures on HOPG*, Kathryn Perrine,*** *M. Trought, I. Wentworth, C. de Alwis, T.R. Leftwich,* Michigan Technological University

Growth of heterogeneous catalysts, plasmonic and other nanostructured materials requires atomic level control and molecular level understanding of the growth of metals and metal oxides on surfaces. Surface functionalization of 2D materials can be used to promote selective nucleation of metal oxides with control over the deposition and growth. However, this requires an understanding of surface functionalization. This surface chemical functionalization can be combined with the atomic-level control of atomic layer deposition (ALD). ALD is a vapor deposition technique that utilizes self-limiting surface reactions to grow metal oxides, where the surface functional group initiates the first step in the deposition process.

2D materials are ideal for selective functionalization that may not require lithography steps due to the fact that their sheets are in a stable configuration making them chemically unreactive. Highly oriented pyrolytic graphite (HOPG) is an ideal model of the graphene surface, a well-known 2D material, which is comprised of sp^2 hybridized aromatic hydrocarbon sheets. HOPG consists of stacked graphene sheets where the terraces of the carbon sheets are chemically unreactive in ambient conditions and their defects are highly reactive. Oxidation methods are used to produce an assortment of different functional groups on HOPG and can lead to different types of functionalities on the surface and its defects.

We investigate how surface oxidative etching and functionalization influences the growth of metal oxide structures at tailored defects and functional sites on HOPG. Two different acids were used to etch the HOPG surface to produce functional groups resulting in different surface topographies. The functionalized HOPG was then exposed to trimethylaluminum and water, a well-known ALD reaction, to produce Al_2O_3 as a proof-of-concept to observe the growth of Al_2O_3 on both functional and defect sites. Vibrational spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to measure surface functionalization and Al_2O_3 growth on HOPG. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectral imaging were used to image the changes in surface topography after etching and ALD deposition. Results indicate that the Al_2O_3 deposition and growth is dictated by the surface functionalization and topography. This suggests that understanding the effects of surface functionalization of 2D materials is necessary for controlling the growth of metal oxide structures.

11:20am **SS+EM+NS-ThM11 Impurity Induced Chemical Properties of BN on Rh(111) Studied by First Principle Calculations: A New Phase*, Zahra Hooshmand*[1]**, *D. Le, T.S. Rahman,* University of Central Florida

Hexagonal boron nitride (h-BN), an insulating layer of sp^2 hybridized structure between B and N, grown on Rh(111) forms a Moiré pattern with elevated (rim) and depression (valley) areas. The valleys are circular dipole rings which act as trapping centers for the adsorption of nanoparticles and molecules [1]. The presence of the native carbon impurities in Rh potentially gives rise to the formation of hexagonal carbon rings under every other rim area as suggested by recent experiments [2] and could lead to new structures and novel chemistry. Here, on the basis of Density Functional Theory (DFT) simulations with dispersion corrections, we show that these rings tend to grow in a manner in which the center of each ring is placed on top of the Rh atom. These rings grow next to each other and form islands which are separated from each other by an equal distance while the BN monolayer remains untouched, i.e. there is no C-B or C-N bond formed. Our calculations show that while no broken bonds between B and N were observed, the increase in the concentration of carbon impurities will enhance the height modulations among different regions of BN Moiré pattern leaving the former valleys unchanged while decreasing their area. The new higher elevated regions show strong accumulation of charge and the lower elevated regions display depletion of charge. This gives rise to modification of dipole rings and results in altered adsorption of pentacene on BN. Our simulations of Scanning Tunneling Microscope (STM) images from this structure, are in good agreement with experimental data for number of rings from 3 to 5. However spatial density of states analysis shows that in the presence of 5 rings islands the gap in BN on the higher elevated regions vanishes and the band gap on these areas for 3 and 4 rings islands reduces. The calculations of local variations in work function also show that these variations become more pronounced by growth of islands and reduces the work function of lower elevated regions in new phase. This results show that by control of the concentration of local impurities underneath the rim areas in BN, the chemical properties are modified and the monolayer could be engineered for interesting chemical reactions. [1] H. Dil et al., *Science*, 2008, 319, 1824-1826. [2] Koslowski et al. Private communication.

This work was supported by National Science Foundation, Grant #NSF CHE-1465105"

---

[1] **National Student Award Finalist**

11:40am **SS+EM+NS-ThM12 Texture of Atomic-layer Deposited MoS: A polarized Raman Study*, Vincent Vandalon*,** *A. Sharma, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands*; A.A. Bol,* Eindhoven University of Technology, Netherlands

Advances in optical characterization techniques for 2D transition metal dichalcogenides (2D-TMDs) such as MoS2 are essential in the context of tailoring the texture and surface functionalization of these materials. Tailoring of the texture of *synthesized* MoS2 results in uniquely different material characteristics: out-of-plane fins of MoS2 have been demonstrated to possess excellent catalytic performance, most likely due to exposed catalytically active edge sites, whereas basal plane oriented MoS2 shows excellent electronic properties. The large impact of texture on the exhibited properties underlines the need for rapid and facile characterization of the texture and especially the angular grain orientation. So far, cross section high-resolution transmission electron microscopy (HR-TEM) is widely employed to obtain insight into texture but it suffers from a limited throughput. On the other hand, Raman spectroscopy has been established as the *go-to* technique for the determination of e.g. film thickness of these TMDs. Here we will show that the angular grain distribution can also be determined using *polarized* Raman spectroscopy

We have found that plasma-enhanced atomic-layer deposition (PE-ALD) of MoS2 allows control over the texture and results in out-of-plane fins or basal plane oriented material depending on the processing conditions using HR-TEM. To study the texture of the PE-ALD synthesized films with Raman spectroscopy, we have investigated the so far unknown impact of the angular grain distribution on the Raman response. The Raman response of nanocrystalline MoS2 was modeled for a range of different textures. This allowed us to determine the angular grain distribution from the peak ratio of the two dominant Raman peaks (i.e. the A1g and E2g modes). Furthermore, the modeling also showed that performing *polarized* variant of Raman spectroscopy is essential for the accurate determination of the angular grain distribution because of the additional information it provides. A systematic polarized Raman study into the evolution of the fraction of out-of-plane material with film thickness allowed us to gain insight into the growth process. Moreover, the influence of a post-deposition high-temperature anneal in a H2S atmosphere on the texture, known to yield improved material properties, was also investigated. To conclude, polarized Raman spectroscopy offers a rapid method to gain insight into the angular grain distribution of synthesized MoS2 and this approach can be readily extended to other MX2 materials.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-ThA

Bridging Gaps in Heterogeneously Catalyzed Reactions

Moderator: Ryan Brown, Clarkson University

2:20pm **HC+SS-ThA1 Hydrogen Adsorption and Reaction on $RuO_2(110)$ Surface***, A. Dahal, I. Lyubinetsky,* ***Zdenek Dohnalek,*** Pacific Northwest National Laboratory

Ruthenium dioxide is used extensively as a co-catalyst in a wide range of photocatalytic water splitting systems. As such, understanding how it promotes the evolution of hydrogen and oxygen is of high importance. In our studies, we employed scanning tunneling microscopy in combination with moleculear beam scattering and temperature programmed desorption studies to follow adsorption, reaction, and thermal evolution of hydrogen on a model $RuO_2(110)$. In our temperature-dependent studies, we find that at low coverages ($H_2/Ru < 0.2$) H_2 dissociates heterolytically and forms hydride-hydroxyl pairs below 100 K. At higher coverages ($H_2/Ru > 0.2$), H_2 adsorbed on Ru sites neighboring the hydride-hydroxyl pairs chemisorbs molecularly. Upon annealing the hydride species convert to hydroxyls and most of the chemisorbed H_2 desorbs. Upon heating, the low and high H_2 covered surfaces transform to partially and fully hydroxylated surface, respectively, above 250 K. Molecular beam scattering studies reveal that the adsorption probability of hydrogen on this surface is strongly temperature-dependent, decreasing from ~0.4 at 25 K to <0.01 at 300 K. These combined studies unravel a complete adsorption and dissociation mechanism of H_2 on this model ruthenium dioxide surface.

2:40pm **HC+SS-ThA2 The Role of Oxides for CO Oxidation over Pd and Rh, and How to Deal with Oxygen Poisoning***,* ***Johan Gustafson,*** Lund University, Sweden*; O. Balmes,* MAX IV Laboratory, Sweden*; C. Zhang,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; A. Schaefer,* Chalmers University of Technology, Gothenburg, Sweden*; B. Hagman,* Lund University, Sweden*; L. Merte, N.M. Martin, P-A. Carlsson,* Chalmers University of Technology, Gothenburg, Sweden*; M. Jankowski,* ESRF, France*; E.J. Crumlin,* Advanced Light Source, Lawrence Berkeley National Laboratory*; E. Lundgren,* Lund University, Sweden

Catalytic CO oxidation is a seemingly simple reaction between CO and O_2 molecules, one of the reactions in automotive catalytic converters, and the fruit-fly reaction in model catalysis. Surprisingly, the phase responsible for the catalytic activity is still under debate, despite decades of investigations. We have performed a simple but yet conclusive study of single crystal Rh and Pd model catalysts, resolving this controversy. For Rh, the oxygen covered metallic surface is more active than the oxide, while for Pd, thin oxide films are at least as active as the metallic surface, but a thicker oxide is less active [1]. The difference between these oxide structures is that the thin PdO films expose coordinatively unsaturated (CUS) metal atoms that act as active sites, while Rh oxides and thicker PdO films do not expose such sites and are hence less active. Similar results have also been found for methane oxidation over Pd [2].

Under highly oxidizing conditions, which are, for instance, desirable for optimal efficiency of combustion engines, there is a general problem of deactivation of catalysts due to too high oxygen exposure, so-called oxygen poisoning. With the above results in mind, this problem is likely related to the formation of oxides that do not expose CUS sites. We therefore believe that the problem of oxygen poisoning over Pd catalysts can be solved by growing a PdO film on top of a more inert metal such as Ag or Au, as this will limit the thickness of the oxide film and hence stabilize the active oxide surface.

In this presentation, we will discuss the active phase of Pd and Rh for CO oxidation, and hopefully show the first results of lower degree of oxygen poisoning for CO and methane oxidation over Pd/Au and Pd/Ag systems.

References

1. J. Gustafson et al., The Role of Oxides in Catalytic CO Oxidation over Rhodium and Palladium, ACS Catal., 2018, *8*, 4438–4445.

2. A. Hellman et al., The active phase of palladiumduring methane oxidation, J. Phys. Chem. Lett. 2012, 3, 678–682.

3:00pm **HC+SS-ThA3 Simplifying the Relationships between Catalyst Structure and Reaction Rates for Complex Mechanisms***,* ***Charles T. Campbell,*** University of Washington **INVITED**

Better catalysts and electro-catalysts are essential for many energy and environmental technologies of the future. Designing better catalysts requires knowing the relationships between catalyst structure and catalytic reaction rates, which are in general poorly understood. I will review here some concepts that clarify and simplify these relationships. While a typical catalytic reaction has a dozen or more adsorbed intermediates and elementary-step transition states, Degree of Rate Control (DRC) analysis can be applied to a microkinetic model of the best known catalyst material to show that the net rate really only depends upon the energies of a few (2 to 4) of these. For related materials, one only needs to know how the change in material affects the energies of these few 'rate-controlling species' to understand how rates relate to structure. This offers opportunities for designing better catalysts. DRC analysis also provides a simple way to predict kinetic isotope effects (KIEs), which can be compared to simple KIE experiments to verify the energy accuracy of a microkinetic model (that is often based on DFT energies). Such DFT energies can be used with DRC values to predict faster catalysts.

The chemical potential of metal atoms (u_m) in supported catalyst nanoparticles provides another simplifying concept for developing structure – rate correlations in catalysis. It has been known for years that this chemical potential enters directly into the rate equations for catalyst deactivation by sintering. I will show here that it also correlates strongly with the strength with which surface metal atoms bind adsorbed reaction intermediates (and transition states), which correlate with rates as outlined above. I will then review what aspects of catalyst structure control metal chemical potential. It can be tuned to lower values (relative to large particles of the pure metal) by mixing the metal with another metal with which it forms an exothermic alloy, and tuned higher by making the nanoparticles smaller and putting them on a support to which they have a smaller adhesion energy (E_{adh}). Quantitative equations that predict how u_m varies with size and E_{adh}, and how E_{adh} depends on the metal element and the oxide surface used as the catalyst support will be presented. These also offer opportunities for predicting faster catalysts.

· Work supported by NSF and DOE-OBES Chemical Sciences Division.

4:00pm **HC+SS-ThA6 Spectroscopic Techniques for Identifying Reactive Intermediate Structures during Decomposition of Formic Acid over Metals and Metal Oxides***,* ***Megan Witzke,*** *D.W. Flaherty,* University of Illinois at Urbana-Champaign

Identifying reactive intermediates within an "organometallic zoo" of species that form on surfaces of metal nanoparticles and metal oxides during reactions is a long standing challenge in heterogeneous catalysis.[1] We use a combination of spectroscopic techniques and data analysis methods to isolate and extract spectral features of the reactive intermediates present under relevant operating conditions. Modulation excitation spectroscopy coupled with phase sensitive detection selectively filters spectra to show only reactive intermediates and suppress features of spectating species.[2] The combined spectra of all reactive species are deconvoluted using singular value decomposition techniques that provide distinct spectra and estimate surface coverages for independent species.[3] Comparisons of spectra obtained at different modulation frequencies exploit differences in intrinsic free energy barriers between reactive intermediates by removing species that are unable to form at higher stimulated frequencies. We combine these techniques to molecularly interpret infrared spectra to identify compositionally similar surface intermediates formed in situ during decomposition of formic acid (HCOOH) over anatase TiO_2 and Au-TiO_2. Operando and transient measurements determine the sequence of elementary steps that decompose HCOOH and identify surface species that do not form CO and CO_2. Transient measurements show that HCOOH adsorbs and deprotonates to form bidentate formates over TiO2 while monodentate intermediates do not lead to CO or CO_2 formation. Selective inhibition of Au sites with co-fed CO over Au-TiO_2 indicate monodentate reactive intermediates evolve into bidentate formates on Au at higher coverages. Distinguishing the structure, composition, and orientation of reactive intermediates provides complimentary evidence to measured rates and DFT to depict reaction mechanisms and provide insight into how surface properties dictate rate and selectivity.

References:

(1) Burwell, R. L. The mechanism of heterogeneous catalysis, C&EN Magazine, 22 August, 1966, 56.

(2) Urakawa, A.; Burgi, T.; Baiker, A. Chem. Eng. Sci. 2008, 63, 4902.

(3) Jaumot, J.; de Juan, A.; Tauler, R. Chemometr. Intell. Lab. 2015, 140, 1.

4:20pm **HC+SS-ThA7 Self-sustained Reaction Oscillations in a New Light***, **Uta Hejral**, S. Albertin, J. Zhou, S. Pfaff,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; S. Blomberg,* Lund University, Sweden*; O. Gutowski, A. Dippel,* Deutsches Elektronen-Synchrotron DESY, Germany*; J. Gustafson, J. Zetterberg, E. Lundgren,* Lund University, Sweden

Catalysts are complex material systems accelerating desired chemical reactions in chemical industry, fuel cells and car exhaust treatment. To improve their performance, an atomic-scale understanding of the interplay between catalyst structure, the surrounding gas composition and the catalyst activity under realistic reaction conditions is inevitable. Self-sustained reaction oscillations, in which the catalyst shuts its activity periodically off, have been studied for many years [1, 2] with the aim (1) to avoid reactor instabilities or even reactor explosions, and (2) to understand and make use of the underlying catalyst structures leading to higher conversion rates and selectivities often present during the oscillations. However, no general mechanism, especially for the structure leading to the activity increase and decrease, has been put forward.

Here we combined High Energy Surface X-Ray Diffraction (HESXRD) [3, 4], Planar Laser Induced Fluorescence (PLIF) [5], in-situ Mass Spectrometry (MS) and optical LED reflectance [6] at beamline P07 (DESY) at a photon energy of 77 keV to study self-sustained reaction oscillations during CO oxidation over Pd(001). This allowed, with sub-second time resolution, for correlating the catalyst structure (HESXRD) to the sample's CO_2 production (PLIF, MS) and hence its catalytic activity. The LED light, reflected from the sample surface, provided in addition immediate information on the surface roughness. Our data indicate that the oxidation and reduction of (111)-oriented Pd islands on top of an epitaxial PdO(101) oxide layer, previously reported under reducing conditions close to UHV [7], play a crucial role in the underlying mechanism for the self-sustained reaction oscillations.

References:

[1] F. Schüth et al., Adv. Catal. **39**, 51 (1993).

[2] B. L. M. Hendriksen et al., Nature Chem. **2**, 730 (2010).

[3] J. Gustafson et al., Science **343**, 758 (2014).

[4] U. Hejral et al., Phys. Rev. B **96**, 195433 (2017).

[5] S. Blomberg et al., J. Phys.: Condens. Matter **28**, 2222 (2016).

[6] J. Zhou et al., J. Phys. Chem. C **121**, 23511 (2017)

[7] J. F. Weaver, ACS Catal. **7**, 7319 (2017).

4:40pm **HC+SS-ThA8 Operando Catalysis--A First-Principles Perspective***, **William Schneider**,* University of Notre Dame **INVITED**

First-principles computational methods have had a profound impact on the science of heterogeneous catalysis. One of the challenges in making these models more rigorous, for instance to establish quantitative relationships between experimental observations of rates, rate orders, and models, is to faithfully account for the influence of the catalytic reaction conditions on the state of a catalytic material and on mechanism. "Operando" experiments interrogate catalysts at the conditions at which they are functioning. In the same way, by incorporating finite temperatures and pressures through statistical mechanical and ab initio dynamics models, and by recognizing that a catalytic material may present a heterogeneous array of sites, it is in principle to model a catalyst "operando" from first principles. In this presentation I first discuss our efforts to model finite-temperature adsorption behavior at metal surfaces, including the translational motions that control adsorption free energies and the interactions between adsorbates that can modify surface reaction kinetics. I then discuss our recent work to describe how the rates of surface reactions might be altered by the imposition of an external plasma, showing how changing the "environment" is an alternative and promising way to control catalytic reactivity.

5:20pm **HC+SS-ThA10 Chiral Selectivity in Heterogeneous Catalysis***, R. Chapleski, **Sharani Roy**,* University of Tennessee Knoxville

Developing powerful next-generation technologies for catalysis, energy conversion, and energy storage relies on understanding and controlling molecular transformations at complex interfaces. However, relatively little is known about the fundamental molecular-scale phenomena driving chemical selectivity at functional and complex interfaces. Our work aims to investigate mechanisms of enantioselectivity in heterogeneous catalysis. Specifically, by investigating hydrogenation reactions of both the (R)- and (S)- enantiomers of limonene on the chiral Pt(532) surface, we will provide insight into the adsorbate-surface interactions that lead to enantiomeric excess in the formation of the chiral product, menthene. Here, we report our initial results of this work, which uses computational methods to probe molecular adsorption of limonene followed by catalytic hydrogenation. Our approach utilizing density functional theory combined with the results of recent experimental sum-frequency generation experiments, reveals likely adsorption orientations and reaction pathways of both enantiomers on the Pt(532) surface. A comparison of adsorption and reaction mechanisms across both enantiomers leads to a fundamental description of the atomic-scale interactions that produce enantioselectivity in adsorption and reactions of limonene on a chiral platinum surface. We hope that these results provide qualitative insight into how enantioselectivity is achieved in heterogeneous catalysis at intrinsically chiral metal surfaces.

5:40pm **HC+SS-ThA11 Combining *in situ* Environmental TEM and Multiscale Simulations to Study the Dynamic Processes of Copper Oxidation***, **Meng Li**, M.T. Curnan, W.A. Saidi, J.C. Yang,* University of Pittsburgh

Cu-based materials are widely used in industrial catalysts applications, including methanol synthesis and H_2 production from the water-gas shift reaction. Across these applications, maximizing the Cu surface area improves the catalytic performance. However, side effects such as poor stability and deactivation also occur due to oxide formation at active sites over long-term use. Therefore, developing a fundamental understanding of the nanoscale mechanisms initiating Cu surface oxidation is essential to addressing these issues. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Of these three stages, the initial stage – which spans from the oxygen chemisorption to the onset of oxide nucleation – is least understood, as it is inaccessible to traditional surface science and bulk material experimental methods. Despite recent improvements in computational methods, current computational capabilities have yet to simulate O chemisorption directly leading to oxide nucleation, given the resources required to complete such simulations over sufficiently large time and size scales.

In this work, by combining Environmental TEM (ETEM) with multiscale atomistic simulation, the dynamical processes enabling initial stage copper oxidation were explored. Our ETEM (Hitachi H-9500, 300 kV, LaB_6) results show that over surface step defects of various facet orientations, oxide nucleation preferences vary over adjacent facet edges, potentially leading to known differences in observed reconstructions on differently oriented surfaces. Surface reconstructions on Cu(100) and Cu(110) facets were observed, followed by Cu_2O island nucleation and growth in a layer-by-layer manner. Investigation of the dynamical processes leading to oxide nucleation on these reconstructed surfaces is done via a multiscale computational approach. Single initial oxidation stage events from oxygen chemisorption to surface reconstruction are first modeled using the Nudged Elastic Band (NEB) method on systems modeled with Reactive Force Field (RFF) potentials. Oxide nucleation and growth is then affordably modeled at size and time scales consistent with ETEM results, applying structures and energies resolved in RFF NEB calculations to rate tables used by adaptive kinetic Monte Carlo simulations. This simulation methodology forms a feedback loop with ETEM results, allowing computational and experimental results to validate one other. Ultimately, this cross-validation will be used to explain how oxide nucleation can be prevented by controlling factors like surface and defect orientation, temperature and pressure.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+HC+SS-ThA

IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.**, ***Klaus Attenkofer***, *E. Stavitski, M. Liu, D. Lu, M. Topsakal, D.J. Stacchiola, M.S. Hybertsen,* Brookhaven National Laboratory **INVITED**

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a “field of view” in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistical relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA3 Soft X-ray Spectroscopy for High Pressure Liquid**, ***Ruimin Qiao***, *J.-H. Guo, W. Chao,* Lawrence Berkeley National Laboratory **INVITED**

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid(up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation**, ***Zongfang Wu***, *H. Kuhlenbeck, W. Schöllkopf, H.J. Freund,* Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the $V_2O_3(0001)/Au(111)$ (~10 nm thick) and a $TiO_2(110)$ single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 µm) IR radiation. For $V_2O_3(0001)/Au(111)$ the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the $TiO_2(110)$ single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA7 Spectroscopic Insight into Resistive Switching Processes in Oxides**, *C. Baeumer, C. Schmitz,* Forschungszentrum Juelich GmbH, Germany; *A. Kindsmüller,* RWTH Aachen University, Germany; *N. Raab, V. Feyer, D.N. Mueller, J. Hackl, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany; *O.T. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy; *R. Waser, R. Dittmann,* ***Claus Michael Schneider***, Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3$(STO) and $ZrO_2$with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

[1] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser and R. Dittmann, Nat Commun **7** (2016) 12398.

[2] A. Kindsmüller, C. Schmitz, C. Wiemann, K. Skaja, D. J. Wouters, R. Waser, C. M. Schneider and R. Dittmann, APL Materials **6** (2018) 046106.

[3] C. Baeumer, R. Valenta, C. Schmitz, A. Locatelli, T. O. Mentes, S. P. Rogers, A. Sala, N. Raab, S. Nemsak, M. Shim, C. M. Schneider, S. Menzel, R. Waser and R. Dittmann, ACS Nano **11** (2017) 692.

4:40pm **SA+AS+HC+SS-ThA8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy**, ***Yulin Chen***, Oxford University, UK **INVITED**

The electronic structure of matter is critical information that determine its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

[1] Science, 325, 178 (2009), Science, 329, 659 (2010), Nature Nanotechnology, 6, 705 (2011), Nature Chemistry, 4, 281 (2012), Nature Physics, 9, 704 (2013), Science, 343, 864 (2014), Nature Materials, 13, 677 (2014), Nature Physics, 11, 728 (2015), Nature Materials, 15, 27(2016), Nature Communications 7, 12924 (2016), Nature Communications, 8, 13973 (2017).

5:20pm **SA+AS+HC+SS-ThA10 Electronic Structure of FeO, γ-Fe_2O_3 and Fe_3O_4 Epitaxial Films using High-energy Spectroscopies**, ***German Rafael Castro,*** Spanich CRG BM25-SpLine Beamline at the ESRF,, France*; J. Rubio Zuazo,* Spanish CRG BM25-SpLine at the ESRF, France*; A. Chainani,* Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China*; M. Taguchi,* RIKEN SPring-8 centre, Japan*; D. Malterre,* Institut Jean Lamour, Universite de Lorraine, France*; A. Serrano Rubio,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ-Fe_2O_3 and Fe_3O_4 films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO6 cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd}, the charge-transfer energy Δ, and the metal-ligand hybridization strength V. The results also provide estimates for the ground state and final state contributions in terms of the d^n, d^{n+1}L1 and d^{n+2}L2 configurations. Both FeO and γ-Fe2O3 can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO6 cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ-Fe_2O_3 and Fe_3O_4. Based on simplified calculations using an M2O7 cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ-Fe_2O_3 and Fe_3O_4.

5:40pm **SA+AS+HC+SS-ThA11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation**, *M.H. Nielsen, J.A. Hammons, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgin, K. Champley, W. Shaw,* Lawrence Livermore National Laboratory*; N. Sinclair,* Washington State University*; **Trevor Willey,*** Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutches is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

Surface Science Division
Room 203C - Session SS+AS+BI+MI+NS-ThA

Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion**, *J.A. Phillips, L.K. Harville, H.R. Morgan, L.E. Jackson, G. LeBlanc, **Erin Iski,*** University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

(1) Iski *et al.* Electrochimica Acta (**2011**), 56, 1652-1661.

(2) Iski *et al. submitted to Communication Chemistry, May 2018.*

2:40pm **SS+AS+BI+MI+NS-ThA2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species**, ***Jeffrey Sayler***, *S. Brown, S.J. 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 such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM 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. Regardless of chain length or even-/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces***, **Janice Reutt-Robey**,* University of Maryland College Park **INVITED**

All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material ($LiCoO_2$ or Li) and a capping film of solid electrolyte ($Li_xAl_2O_3$ or Li_20), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cotrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

4:00pm **SS+AS+BI+MI+NS-ThA6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111) √3×√3-Ag Surface***, **Renjie Liu**,* Lakehead University, Canada*; C. Fu, A.G. Moisseev, M.R. Rao, Y. Chen, D.F. Perepichka,* McGill University, Canada*; M.C. Gallagher,* Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111) √3×√3-Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)-√3×√3-Ag surface. The self assembly of TIPT on HOPG and Au(111) has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the √3-Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant interaction within the domains is intermolecular I···H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder. STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying √3-Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br···Br interactions. With increasing coverage, the √3 surface remains unaffected and the self assembled layer extends over the entire surface.

[1] Yokoyama, T. *et al.*, *J Chem Phys* **142**, 204701 (2015).

[2] Gatti, R. *et al.*, *J. Phys. Chem. C* **118**, 25505–25516 (2014).

[3] Nakatsuka, S. *et al.*, *Angewandte Chemie* **129**, 5169–5172 (2017).

4:20pm **SS+AS+BI+MI+NS-ThA7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111)***, **Jodi Grzeskowiak**,* University at Albany-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

4:40pm **SS+AS+BI+MI+NS-ThA8 Measuring the Electronic Properties of Organic Single Crystals***, **Sujitra Pookpanratana**, E.G. Bittle, C.A. Hacker, S.W. Robey,* National Institute of Standards and Technology (NIST)*; R. Ovsyannikov, E. Giangrisostomi,* Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the "fundamental" electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNTT). DNTT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching 10 $cm^2/(V\ s)$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNTT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic "band" structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNTT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and this result will be discussed in context of the charge carrier behavior of DNTT reported in the literature.

[1] J. Ivanco et al., Adv. Mater. 15, 1812 (2003)

[2] S. Krause et al., Org. Electron. 14, 584 (2013)

[3] W. Xie et al., Adv. Mater. 25, 3478 (2013)

[4] U. Zschieschang et al., Adv. Mater. 22, 982 (2010)

[5] N. K. Za'aba et al., Org. Electron. 45, 174 (2017)

5:00pm **SS+AS+BI+MI+NS-ThA9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition***, **Christine Cheng**, M. Gupta,* University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhyodrophobicty of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

5:20pm **SS+AS+BI+MI+NS-ThA10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation***, **William DeBenedetti**[1], E.S. Skibinski, M.A. Hines,* Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO_2 functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

5:40pm **SS+AS+BI+MI+NS-ThA11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode***, **Venkateshkumar Prabhakaran**,* Physical Sciences Division, Pacific Northwest National Laboratory*; M.H. Engelhard, A. Martinez,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; G.E. Johnson,* Physical Sciences Division, Pacific Northwest National Laboratory*; S. Thevuthasan,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; V. Murugesan,* Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies, evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity associated with diverse and correlated processes within SEI layer.[1-4] Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion ($TFSI^-$) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

References:

1. Johnson, G. E.; Hu, Q.; Laskin, J., Soft landing of complex molecules on surfaces. *Annual Review of Analytical Chemistry* **2011,***4*, 83-104.
2. Prabhakaran, V.; Mehdi, B. L.; Ditto, J. J.; Engelhard, M. H.; Wang, B.; Gunaratne, K. D. D.; Johnson, D. C.; Browning, N. D.; Johnson, G. E.; Laskin, J., Rational design of efficient electrode–electrolyte interfaces for solid-state energy storage using ion soft landing. *Nature Communications***2016,***7*, 11399.
3. Prabhakaran, V.; Johnson, G. E.; Wang, B.; Laskin, J., *In situ* solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces. *Proceedings of the National Academy of Sciences* **2016,***113*, 13324-13329.
4. Gunaratne, K. D. D.; Johnson, G. E.; Andersen, A.; Du, D.; Zhang, W.; Prabhakaran, V.; Lin, Y.; Laskin, J., Controlling the Charge State and Redox Properties of Supported Polyoxometalates via Soft Landing of Mass-Selected Ions. *Journal of Physical Chemistry C* **2014,***118*, 27611-27622.

Surface Science Division
Room 102A - Session SS+EM+PS+TF-ThA
Deposition, Etching and Growth at Surfaces

Moderator: Bruce E. Koel, Princeton University

2:20pm **SS+EM+PS+TF-ThA1 Controlled Deposition and High-Resolution Analysis of Functional Macromolecules in Ultrahigh Vacuum***, **Giovanni Costantini**,* University of Warwick, UK **INVITED**

The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process.

This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can by studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

---

[1] **National Student Award Finalist**

3:00pm **SS+EM+PS+TF-ThA3 Unconventional Nucleation and Growth Kinetics: *in situ* Variable-temperature Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of Inorganic Monolayers on Metallic Substrates*, Pedro Arias,*** University of California, Los Angeles*; A. Abdulslam,* Colorado School of Mines*; A. Ebnonnasir,* University of California at Los Angeles*; C.V. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California, Los Angeles

The growth of thin films from atoms and/or molecules deposited from the gas phase onto solid substrates is a non-equilibrium phenomenon where the structure, composition, and crystallinity of the films are determined by kinetic and thermodynamic processes. Over the past few decades, vast and fruitful efforts have been devoted to understanding the kinetics of thin film growth. As a result, conventions of the kinetic factors have been developed to predict the growth mechanism and, hence, microstructure of the as-grown films: for example, nucleation at terraces (steps) is expected to occur when surface diffusion of adsorbed species is significantly lower (higher) compared to the deposition flux and is observed at higher (lower) fluxes and lower (higher) substrate temperatures. Here, we report an unconventional growth mode of inorganic monolayers on metallic substrates.

Using in situ ultra-high vacuum scanning tunneling microscopy (UHV STM), we investigated the chemical vapor deposition (CVD) kinetics of hexagonal boron nitride (hBN) monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. We find that the rates of areal coverage and island density increase ten-fold with increasing borazine pressure from 10^{-7} to 10^{-6} Torr at 573 K and three-fold with increasing temperature from 573 K to 673 K and borazine pressure of 10^{-7} Torr. Our STM images reveal an unusual nucleation and growth mode: at lower deposition flux and higher temperature, islands form on terraces; increasing the flux and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the step-edge growth of borazine islands is observed on *both* up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

3:20pm **SS+EM+PS+TF-ThA4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts*, Tobias Morris,*** Indiana University*; D.L. Wisman,* Indiana University, NAVSEA Crane*; I.J. Huerfano, N.A. Maciullis, K.G. Caulton, S.L. Tait,* Indiana University

The utilization of single-site transition metal centers at surfaces is of growing interest in the heterogenous catalysis community. One advantage of single-site metal centers is the high dispersion so that a much higher fraction of atoms contribute to chemical activity compared to nanoparticle catalysts. Our approach to forming single-site metal centers is on-surface complexation with a redox-active ligand, which allows a high degree of ordering on the surface as well as intimate chemical contact of the metal center with the support surface. The ligand design enables us to tailor the coordination geometry and oxidation state of the metal and thus affect the cooperation between metal and ligand and the chemical reactivity. Several ligands, differing in backbone, binding pocket, design, and peripheral units were examined in this study. Tetrazine-based ligands are known for their redox activity. The on-surface two-electron redox process utilizes vapor deposition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) with vanadium cations onto an Au(100) surface. The metal-organic complexation leads to the growth of 1D chains consistent of one metal per ligand due to the divergent binding pockets created by the tetrazine core and pyridine rings. Exposing the V-DPTZ chains to oxygen results in a dissociative reaction of molecular oxygen to form a terminal oxo species on the vanadium, while allowing the metal-organic complex to remain intact. Interestingly, the dioxygen activation contributes adsorbed oxygen to the support surface by a spillover mechanism. The stable V-oxo species is the only oxidation product, unlike the unselective oxidation of V nanoparticles. A newly synthesized ligand, tetraethyltetra-aza-anthraquinone (EtTAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. Quinones are one of the oldest studied redox-active ligands. EtTAAQ has the capacity for up to a four-electron reduction, enabling the possibility for multiple metal sites per ligand. Continued work on redesigning ligands is showing promise in increasing the cooperativity of the ligand and the metal which could lead to heightened reactivity.

4:00pm **SS+EM+PS+TF-ThA6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization*, Ross Edel,*** *T. Grabnic, B. Wiggins, S.J. Sibener,* University of Chicago

Graphite is widely studied due to its importance in high-performance materials applications such as high velocity flight systems as well as its key role as a model system for other carbonic materials such as graphene and carbon nanotubes. Our research focuses on the reaction of highly oriented pyrolytic graphite (HOPG) with molecular oxygen, the mechanism of which is not yet fully understood. Utilizing a one-of-a-kind instrument that combines a supersonic molecular beam and scanning tunneling microscope (STM) in ultra-high vacuum, we are able to tightly control the energy and angle of impinging oxygen and examine the nanoscopic and mesoscopic evolution of the surface. We have found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. The faceted and circular etch pits were formed at low O_2 energy, with faceting only apparent below a critical surface temperature, while anisotropic etching was observed with exposure to higher energy oxygen. Comparison of low- and high-grade reacted samples show that anisotropic channels likely result from the presence of grain boundaries. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Reactivity was enhanced by natural grain boundaries and artificially created point defects, showing the critical influence of small structural imperfections. Our combination of STM imaging with well-defined and controlled oxidation conditions connects interfacial reaction kinetics with time-evolving nanoscopic surface morphology, providing new insight into the oxidation of graphitic materials under high-temperature conditions. Spatio-temporal correlations obtained in this manner shed new light on interfacial erosion mechanisms, and provide an incisive complement etch the information obtained using spatially-averaged gas-surface reactive scattering measurements.

5:00pm **SS+EM+PS+TF-ThA9 DLC Films by Modified HiPIMS with Effect from Pulse Parameters on Plasma Parameters and Film Quality*, David Ruzic,*** *I. Haehnlein,* University of Illinois at Urbana-Champaign*; B. Wu,* Southwest Jiaotong University*; D. Barlaz,* University of Illinois at Urbana-Champaign*; B.E. Jurczyk,* Starfire Industries

Diamond like carbon (DLC) films have made waves as of late in many industries. DLC provides a high strength low friction surface with the potential for high chemical resistivity. High Power Impulse Magnetron Sputtering (HiPIMS) is a promising physical vapor deposition (PVD) that creates high ionization fractions at the substrate using high power pulses over low duty factors. The resulting high plasma densities (as high as 10^{19} m^{-3}) creates ionization fractions of sputtered material at the target surface. The increase in energy of atoms due to high ionization rates at the substrate yields higher density and smoother films. In combination with a positive polarity pulse to drive ions to the substrate surface, the DLC film hardness can be increased while producing a smoother film surface.

By introducing a larger ion flux, determined through a gridded energy analyzer, the ratio of sp^3 bonded carbon to sp^2 is presented for a multitude of parameters. This work explores not only the use of positive polarity pulses, but the effect of pulse parameters, has on film hardness and morphology. By controlling the deposition rate through pulse width and repetition rate while controlling deposition energy increases by approximately 5% in sp^3 fraction were observed while surface roughness decreased by a factor of 4 for a non-hydrogenated amorphous carbon film by just the introduction of a positive polarity pulse. Further increases are reported through fine tuning the discharge parameters while looking at plasma densities, ion fraction, surface roughness, sp^3 fraction, and hardness for DLC on silicon substrates.

5:20pm **SS+EM+PS+TF-ThA10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering*, Haoshan Zhu*[1]*,*** *W. Zhou, J.A. Yarmoff,* University of California - Riverside

Bi_2Se_3 and Bi_2Te_3 are two-dimensional topological insulators (TIs) that have attracted intense interest in recent years. TIs are promising candidates for superconductor, spintronics and quantum computing applications due to topological surface states (TSS) that connect the conduction and valence bands. The clean $Bi_2(Se,Te)_3$ surfaces prepared under ultra-high vacuum

---

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

(UHV) are terminated with Se or Te, but the termination can change if exposed to air or prepared under non-ideal conditions. The adsorption and reactions of various atoms and molecules with $Bi_2(Se,Te)_3$ have thus been studied extensively, as they can result in changes to the TSS, doping and surface reconstruction. Here, TI surfaces are exposed to Cs, Bi, and halogens (Cl_2 and Br_2) in UHV and investigated by low energy electron diffraction (LEED), work function measurements and low energy ion scattering (LEIS). It is found that Cs lowers the work function and remains stable at small coverages but becomes mobile at larger coverages. Bi grows in a quasi bilayer-by-bilayer mode with the first Bi bilayer being strongly bonded to the TI surface. Both clean TI surfaces and Bi-covered surfaces are exposed to halogens. The clean surfaces are relatively inert to halogens, but they readily adsorb onto Bi films . The Bi is etched away when the samples are lightly annealed, restoring the clean Se- or Te-terminated surfaces.

5:40pm **SS+EM+PS+TF-ThA11 Atomically Controlled Metallation of Porphyrinoid Species with Lanthanides on Surfaces***, **Borja Cirera,*** IMDEA Nanoscience, Spain*; J. Björk,* Linköping University, Sweden*; G. Bottari, T. Torres,* Universidad Autonoma Madrid, Spain*; R. Miranda, D. Ecija,* IMDEA Nanoscience, Spain

Metallation of surface confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis.

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing different backbones, is attracting great attention. In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal for magnetic applications, of porphyrinoid species of distinct cavity size.

On one hand, the deposition of Dy on top a submonolayer of fluorinated tetraphenyl porphyrin species on Au(111) affords the expression of three different Dy-derived compounds, which are identified as the: initial, intermediate and final metallated states. Importantly, the initial metallated complexes exhibit a narrow zero bias resonance at the Fermi level that is assigned to a molecular Kondo resonance with $T_k \approx 120$ K, which can be switched off by means of vertical manipulation.

On the other hand, the adsorption on Au(111) of an expanded hemiporphyrazine with 27 atoms in its internal cavity is investigated, showing a long-range orientational self-assembly. Furthermore, a spatially controlled "writing" protocol on such self-assembled architecture is presented, based on the STM tip-induced deprotonation with molecular precision of the inner protons. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif.

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface patterning, opening new avenues for molecular level information storage, and boosting the emerging field of surface-confined coordination chemistry involving f-block elements.

Thin Films Division
Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA

IoT Session: Thin Films for Flexible Electronics and IoT

Moderators: Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA1 Ultraflexible Organic Electronics for Bio-medical Applications***, **Tomoyuki Yokota,** T. Someya,* The University of Tokyo, Japan **INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

References

[1] D. Khodagholy et al., Nature Commun. **4** 1575 (2013).

[2] G. Schwartz et al., Nature Commun. **4**, 1859 (2013).

[3] L. Xu et al., Nature Commun. **5** 3329 (2014).

[4] D. H. Kim et al., Nat. Mater., **9**, 511 (2011).

3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics***, **Jacob W. Ciszek**,* Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment***, **Tony Maindron**, S.M. Sandrez, N.V. Vaxelaire,* CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO_2 ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In_2O_3:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy**, *Y. Wu, B. Macco,* Eindhoven University of Technology, The Netherlands*; A.D. Giddings, T.J. Prosa, D.J. Larson,* CAMECA Instruments Inc.*; S. Kölling, P.M. Koenraad, F. Roozeboom,* ***Erwin Kessels****, M.A. Verheijen,* Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of $Zn(C_2H_5)_2$ and H_2O with cycles of $Al(CH_3)_3$ and H_2O in a supercycle fashion at 250 ºC. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called "ALD supercycles" is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In_2O_3:H prepared by InCp and a mixture of O_2 and H_2O at 100 ºC. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 ºC. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition o ccurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D_2O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

[1] Y. Wu, A. Giddings, M.A. Verheijen, B. Macco, T.J. Prosa, D.J. Larson, F. Roozeboom, and W.M.M. Kessels, Chem. Mater. 30, 1209 (2018).

[2] Y. Wu, B. Macco, D. Vanhemel, S. Kölling, M.A. Verheijen, P.M. Koenraad, W.M.M. Kessels, and F. Roozeboom, ACS Appl. Mater. Interfaces, 9, 592 (2017).

4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier**, ***Kai Zhang****,* University of Oxford, Department of Materials, UK*; C.-M. Chen, B. Choubey, H.E. Assender,* University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

Reference:

DING, Z., ABBAS, G. A. W., ASSENDER, H. E., MORRISON, J. J., YEATES, S. G., PATCHETT, E. R. & TAYLOR, D. M. 2016. Vacuum production of OTFTs by vapour jet deposition of dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) on a lauryl acrylate functionalised dielectric surface. *Organic Electronics,* 31**,** 90-97.

TAYLOR, D. M., PATCHETT, E. R., WILLIAMS, A., DING, Z., ASSENDER, H. E., MORRISON, J. J. & YEATES, S. G. 2015. Fabrication and simulation of organic transistors and functional circuits. *Chemical Physics,* 456**,** 85-92.

4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors**, *X. Du, S. John, J. Bergevin,* ***Gregory Herman****,* Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters.These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors**, *C. Frijters, I. Katsouras, A. Illiberi, G. Gelinck,* Holst Centre / TNO, Netherlands*;* ***Paul Poodt****,* Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with $InZnO_x$ (IZO) and $InGaZnO_x$ (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N_2/O_2 plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD rector. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V_{on} and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics***, **Jesse Jur**, I. Kim, H. Shahariar,* North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics***, **Bryan Stuart**, T. Cosnahan, A.A.R. Watt, H.E. Assender,* University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*SeeSupplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min^{-1} showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min^{-1}, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

References

1. Cosnahan, T., A.A. Watt, and H.E. Assender, *Modelling of a vacuum metallization patterning method for organic electronics.* Surface and Coatings Technology, 2017.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures***,* ***Michael F. Crommie,*** University of California at Berkeley Physics Dept. **INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces***,* ***Christopher Goodwin,*** University of Delaware*; A.J. Maynes,* Virginia Polytechnic Institute and State University*; Z.E. Voras,* University of Delaware*; S.A. Tenney,* Center for Functional Nanomaterials Brookhaven National Laboratory*; T.P. Beebe,* University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure if the resulting films, scanning tunneling microscopy and evaluation of valance band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy***,* ***Tomasz Michnowicz,*** Max Planck Institute for Solid State Research, Germany, Deutschland*; B. Borca,* Max Planck Institute for Solid State Research, Germany*; R. Pétuya,* Donostia International Physics Centre, Spain*; M. Pristl, R. Gutzler, V. Schendel, I. Pentegov, U. Kraft, H. Klauk,* Max Planck Institute for Solid State Research, Germany*; P. Wahl,* University of St Andrews, UK*; A. Arnau,* Donostia International Physics Centre, Spain*; U. Schlickum, K. Kern,* Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy***,* ***Giovanni Costantini,*** University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution***,* ***Seong Heon Kim,*** Samsung Advanced Institute of Technology, Republic of Korea*; S.Y. Park, H. Jung,* Samsung Advanced Institue of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, Nano Energy 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Surface Science Division
Room 203C - Session SS+AS+HC-FrM
Near/Ambient Pressure and Bridging Gaps between Surface Science and Catalysis

Moderators: Donna Chen, University of South Carolina, Janice Reutt-Robey, University of Maryland College Park

8:20am **SS+AS+HC-FrM1 Ambient Pressure Electron Spectroscopy (XPS, XAS) and Electron Microscopy Studies of the Structure and Chemistry of Nanostructured Model Catalysts*, John Hemminger*,** University of California Irvine **INVITED**

We use physical vapor deposition to create a high density of metal oxide nanoparticles on highly oriented pyrolytic graphite (HOPG). Photoelectrochemical methods are then utilized to selectively decorate the metal oxide nanoparticles with transition metal nanoparticles. This talk willl describe our studies of the Pt/TiO$_2$/HOPG ; Cu/ZnO/HOPG systems. The nanostructured surfaces are characterized by SEM, TEM, XPS, and synchrotron based XAS. Lab-based and synchrotron based ambient pressure XPS experiments have been used to study the CO oxidation reaction on Pt/TiO$_2$/HOPG and the CO$_2$ reduction reaction on CuO$_x$/TiO$_2$/HOPG. In addition, the catalytic activity of CuO$_x$/TiO$_2$/HOPG for electrochemical CO$_2$ reduction has been studied using differential electrochemical mass spectrometry (DEMS).

9:00am **SS+AS+HC-FrM3 *In-operando* Investigation of the Initial Oxidation Stages for NiCr-(W) Alloys with X-ray Photoelectron Spectroscopy*, Cameron Volders*,** *V. Angelici Avincola, P. Reinke,* University of Virginia

Ni-Cr alloys are of technical interest as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation, and limits catastrophic events such as pitting and crevice corrosion. A wide range of Ni-Cr alloys have been developed to satisfy industrial needs and the properties for each alloy differ slightly based on its application. The properties are controlled by manipulating Cr content as well as adding minor alloying elements such as Mo or W, which have been shown to enhance corrosion resistance. The ideal composition for these alloys has been optimized over many decades but the mechanistic understanding of the role of Mo or W additions is not fully developed.

The current work presents an *in-operando* ambient pressure – X-ray photoelectron spectroscopy (AP-XPS) study which investigated the early stages of oxidation for four alloy concentrations; (1) Ni-5% Cr, (2) Ni-15% Cr, (3) Ni-30% Cr, and (4) Ni-15% Cr-6% W by weight percent between 573 and 773 K and p(O$_2$)< 0.1mbar. The primary objectives were to elucidate how varying Cr content in the alloys and the addition of W impacts the nucleation and growth of different oxide phases. The modulation of alloy and oxide composition and bonding was observed over an extended time period delivering a detailed view of the reaction pathways.

A key result from this work is the Cr surface segregation in the alloys prior to oxidation, which contributes to the rapid nucleation of Cr-oxides in the first reaction step with O$_2$. The surface enrichment of Cr influences the initial nucleation of the different oxide species and prejudices the progression of oxide growth. The main portion of this work will focus on the time evolution of the different oxide phases and the kinetics of Ni-oxide and Cr-oxide formation for all alloys, which allows to build a detailed model of the reaction. An additional component accounts for a substantial portion of the oxide signal, and is interpreted as the combination of spinel and non-stoichiometric oxide. The addition of W in the alloy resulted in a near complete suppression in the formation of Ni oxide species, and different models to interpret the impact of W on the progression of the oxidation reaction will be discussed.

9:20am **SS+AS+HC-FrM4 Surface Hydroxylation of Polar (000-1) and Non-polar (11-20) ZnO Probed with AP-XPS*, Sana Rani*,** *A. Broderick, J.T. Newberg,* University of Delaware

The interaction of ZnO with water vapor has been an important topic of research due to the relevance for numerous catalytic processes including water-gas shift reaction, methanol synthesis, olefin hydrogenation, and gas sensor applications. ZnO based humidity nanosensors were found to have high sensitivity towards humidity and fast response time in heterogeneous catalysis. The presence of water strongly modifies the surface properties depending on the substrate and coverage. The adsorbed water can catalyze heterogeneous reactions and corrosion by proton transfer and solvating products. Dissociation of adsorbed water is of particular interest for catalysis, as this may be the first step in the activation of water molecules for chemical reactions. In this work, surface thermodynamic calculations were applied to synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data to investigate the interface between water vapor and the low index polar (000-1) and non-polar (11-20) ZnO surfaces. Three isobaric experiments were performed over a range of temperatures from 10 to 500°C. It is hypothesized that observed hydroxyl groups, adsorbed water and carbonates on the ZnO surface can significantly influence heterogeneous catalytic reactions under ambient conditions.

9:40am **SS+AS+HC-FrM5 Reason of High Stability and Reactivity of Ni/silicalite-1 Catalyst for Dry Reforming of Methane*, Evgeny Vovk*,** *X. Zhou, Z. Liu, C. Guan, Y. Yang,* ShanghaiTech University, China*; W. Kong,* Shanghai Advanced Research Institute, China*; R. Si,* Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chaina

Dry reforming of methane (DRM) is an environmentally favored process transferring two greenhouse gases (CH$_4$ and CO$_2$) into syn-gas (H$_2$+CO). Ni-based catalysts demonstrate good potential in this application because of comparable reactivity and low cost. DRM is highly endothermic reaction which requires high operating temperatures. At high temperatures sintering is a common issue of catalyst deactivation. Deactivation of Ni catalyst in DRM process is also accompanied by carbon deposition (coking) induced by methane decomposition and CO disproportionation (Boudouard reaction).

In the current work we investigated catalyst obtained by encapsulating Ni clusters (2.5±0.2 nm) into microporous silicalite-1 (aluminum free zeolite with MFI structure). No deactivation and coking under a wide range of conditions where carbon formation is thermodynamically favorable were observed for this sample. This atom-economical Ni/silicalite-1 catalyst was compared with Ni/SiO$_2$ catalyst prepared by impregnation method. XPS study has been performed in ThermoFischer ESCALAB 250X photoelectron spectrometer. The gas treatments of catalysts (up to 1 bar) was performed in high pressure gas cell (Model HPGC 300, Fermi Instruments) connected to the spectrometer.

XPS analysis of Ni/silicalite-1 demonstrates the presence of a peak with binding energy (BE) 856.2 eV in Ni 2p$_{3/2}$ region. Nickel silicate has a similar spectrum shape with close BE. The presence of this peak in Ni/silicalite-1 sample suggests of the Ni-O-Si species and strong metal-support interaction. After oxidation of this sample at 400°C there are no changes of the Ni-O-Si species. At the same time nickel in Ni/SiO$_2$ catalyst which has shown mostly metallic Ni^0 state with minor content of Ni-O-Si upon oxidation transforms into NiO. Reduction of Ni/silicalite-1 catalyst in hydrogen at 650°C leads to partial reduction of nickel into Ni^0 while a significant portion of Ni-O-Si still remains. The behavior of Ni-O-Si feature in both oxidizing and reducing conditions clearly indicates its very high stability. We attribute this feature to the Ni-O-Si formed at the interface between Ni nanoparticles and the silicalite support. The Ni/silicalite-1 novel oxygen-philic interfacial catalyst system consists of very small metallic Ni clusters intercalated into silicalite framework and surrounded by Ni-O-Si species. Ni-O-Si provides high stability of Ni nanoparticles and prevents sintering and carbon deposition making this catalyst also very interesting for commercial application.

10:00am **SS+AS+HC-FrM6 Recent Development in XPS and Ambient Pressure XPS Techniques*, Lukasz Walczak*,** PREVAC sp. z o.o., Poland

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressurephotoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

References

[1] B. Lassalle-Kaisera et al . J. Electron Spectrosc. Relat. Phenom. 221, 18-27 (2017).

[2] Y. Takagi et al. Phys.Chem.Chem.Phys. 19, 6013 (2017).

[3] Z. Y. Ong el. al, Appl. Mater. Interfaces 9, 39259–39270 (2017)

[4] L. K. Preethi el al. Energy Technol., 5, 1-10 (2017)

[5] Urszula Filek el. al, Appl. Catal. A – submitted

10:20am **SS+AS+HC-FrM7 Quantum Mechanics and Reaction Kinetics Study on SiO_2 and SiN Dry Isotropic Chemical Etching Process***, **Taiki Kato,** M. Matsukuma, K. Matsuzaki, L. Chen,* Tokyo Electron Technology Solutions Limited, Japan

Dry isotropic chemical etching processes are important for semiconductor manufacturing, but such processes often require subtle process tuning to achieve high etching rates and the desired etching selectivity between SiO_2 and SiN. For example, the dry chemical etching solely with HF gas (Process 1) requires fine tuning of conditions for SiN etching rate because it has a peaky dependence on the process temperature; whereas dry chemical etching with NH_3/HF binary gas mixtures (Process 2) requires subtle tuning to simultaneously maximize etching rate and SiO_2:SiN selectivity. Notably, in Process 2, SiN etching rate increases with the etching time while SiO_2 etching rate slows down with the etching time. This slowdown is attributed to the formation of an etchant diffusion barrier from the solid byproduct, AFS (Ammonium fluorosilicate). Because of these contradictions, it has been difficult to achieve highly selective and rapid SiO_2 etching, thus a better understanding of the etching mechanisms is important to further develop the high selectivity required for the formation of scaled multicomponent semiconductor device structures. This study therefore focuses on revealing these mechanisms by using the quantum mechanics and by the analysis of reaction kinetics.

Firstly, Process 1 was studied with a quantum mechanical analysis by using the GRRM (Global Reaction Route Mapping) program. For this study, GRRM searched possible etching reaction paths automatically. From this reaction path search, it was revealed that SiN etching by HF gas, when used by itself, is much more rapid than SiO_2 etching. Further analysis was conducted by the reaction kinetics analysis. The kinetics parameters comprised HF adsorption, desorption and etching reactions. This model shows good agreement with the experimental SiN etching behavior.

Moreover, Process 2 was studied with similar quantum mechanics and kinetics analyses. Quantum mechanics analysis revealed that NH_3 combined with HF enhances both SiO_2 and SiN etching reactions. An NH_4F etching model was then added to the kinetics model. Because the etching byproduct, AFS, may be both an SiN etching accelerator and an SiO_2 etching decelerator, we could model the SiN etching kinetics initiated by NH_4F and propagated by NH_4F + AFS. This model quantitatively agrees with the experimental SiN etching data. Likewise, the SiO_2 kinetics model is composed of NH_4F etching, the diffusion resistance through solid AFS and the sublimation of AFS. This model also shows good agreement with experiment.

These analyses reveal the chemical etching mechanisms and enable process optimization. Further discussion will be presented on AVS 65th.

10:40am **SS+AS+HC-FrM8 Viscosity and Surface Tension Effects on Metal Sputtered onto Low Vapor Pressure Liquids***, **Mark De Luna,** M. Gupta,* University of Southern California

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index