

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 Saylor, 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 (LiCoO₂ or Li) and a capping film of solid electrolyte (Li_xAl₂O₃ or Li₂O), 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-Cottrellian 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. Moiseev, 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

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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 (DNNT). DNNT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching $10 \text{ cm}^2/(\text{V s})$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNNT 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-DNNT, 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 DNNT 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 superhydrophobicity 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 DeBenedetti¹, 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 TiO₂ 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

¹ National Student Award Finalist

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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:

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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.

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