

Surface Science Division
Room: 109 - Session SS1-MoA

Selectivity and Reactivity of Chemisorbed Species
Moderator: A.J. Gellman, Carnegie Mellon University

2:00pm SS1-MoA1 **Observation and Modeling of Chiral Modifier-Substrate Complexes on Pt(111)**, *B. Hammer*, Aarhus University, Denmark, *V. Demers-Carpentier*, *P.H. McBreen*, Université Laval, Quebec, Canada **INVITED**

We present a combined density functional theory (DFT) and scanning tunneling microscopy (STM) study of the complex formation between the chiral modifier naphthylethylamine (NEA) and the model substrate trifluoroacetophenone (TFAP) on a Pt(111) surface. The two molecules interact via a hydrogen bond between the amine group on the NEA and the carbonyl on the TFAP. Many different realizations of the hydrogen bond exist depending on the relative position and orientation of the two molecules. However, only very few are observed experimentally. These are all among the most stable structures found in DFT. The chemisorbed TFAP is prochiral and hydrogenation of the carbonyl would lead to a chiral product. The prochirality of TFAP when forming a complex with NEA is regiospecific, i.e., it depends on the position at which the TFAP is chemisorbed relative to the NEA. The origin of this regiospecificity is discussed.

2:40pm SS1-MoA3 **Enantiospecific Decomposition of Tartaric Acid on Spherically Curved Copper Single Crystals**, *B. Holsclaw*, *P. Kondratyuk*, *A. De Alwis*, *A. Reinicker*, *V. Pushkarev*, *A.J. Gellman*, Carnegie Mellon University

The kinetics and mechanisms of many catalytic surface reactions depend on the atomic level structure of surfaces. Detailed study and understanding of the influence of surface structure on a given reaction is experimentally arduous. The space of possible surface orientations spans a two-dimensional continuum. A detailed study of structure sensitive surface chemistry requires preparation and study of many different single crystal substrates, each with a different orientation. A new high-throughput methodology has been developed based on the use of Surface Structure Spread Single Crystals (S4C), spherically curved single crystals that expose a continuous distribution of different crystallographic planes across their surfaces. These S4C surfaces are being studied using surface analysis tools capable of spatially-resolved measurements that can sample the continuous space of surface orientations.

Six copper S4C surfaces have been produced in-house: three low Miller index centered surfaces, (100), (110), and (111); and three high Miller index surfaces, (821), (861), and (432). Each surface has been chosen and spherically curved so that the complete set of surfaces spans the entire stereographic triangle. The surfaces have been characterized using laser profilometry and oriented using x-ray diffraction and low energy electron diffraction. A benefit of the S4C surfaces is that they are naturally chiral, forming regions of either R- or S- chirality. The surface chemistry of a chiral molecule, such as tartaric acid, on a naturally chiral surface can be enantiospecific. Tartaric acid decomposition from copper surfaces shows very high enantioselectivity due to its highly nonlinear surface explosion kinetics. The nature and magnitude of the enantioselectivity of tartaric acid decomposition across the stereographic triangle is not currently well-understood. Copper S4C surfaces provide an opportunity to study tartaric acid decomposition on virtually all possible copper surface structures. This research is the first attempt to map surface enantioselectivity for any compound across the entire stereographic triangle in high detail.

3:00pm SS1-MoA4 **Reaction Pathways of Alcohols with Transition Metal Oxides: A Comparison between WO_3 and MoO_3** , *Z.J. Li*, *Y.K. Kim*, *R.J. Rousseau*, *B.D. Kay*, *Z. Dohnálek*, Pacific Northwest National Laboratory

The reactions of C1-C4 aliphatic alcohols over cyclic $(\text{WO}_3)_n$ and $(\text{MoO}_3)_n$ (n ranges from 3 to 6) clusters were studied experimentally and theoretically using temperature-programmed desorption, infrared reflection-absorption spectroscopy, and density functional theory. Three reaction channels, dehydration, dehydrogenation, and condensation, have been identified on $(\text{WO}_3)_3$ clusters while only dehydration and dehydrogenation have been observed on $(\text{MoO}_3)_n$. The desorption temperature of reaction products decreases with increasing alkyl chain length. The lack of a condensation channel on $(\text{MoO}_3)_n$ is attributed to the lower reactivity of alcohols with $(\text{MoO}_3)_n$ as compared to $(\text{WO}_3)_3$ and consequently a negligible

concentration of the Mo(VI) centers coordinated with two alkoxy species required for this reaction are formed. DFT calculations provide a detailed explanation for the reactivity and relative selectivity among the reaction channels and W(VI) and Mo(VI) metal centers.

This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences, and was performed at EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for the U.S. DOE by Battelle Memorial Institute under contract no. DE-AC06-76RLO 1830. Computational resources were provided at EMSL and the National Energy Research Scientific Computing Center at Lawrence Berkeley National Laboratory.

3:40pm SS1-MoA6 **Molecular Dynamics Simulations of Oligomer Film Stabilization through Ion-Beam Deposition**, *T. Kemper*, University of Florida, *D. Lee*, Lawrence Livermore National Laboratory, *S.R. Phillpot*, *S.B. Sinnott*, University of Florida

Ion-beam deposition is used to stabilize conducting oligomer films for use in organic photovoltaic devices. The goal is to prevent structural changes caused by chemical attack, disorder, or desorption, that are known to degrade device performance. The second-generation reactive empirical bond-order (REBO) potential has been successfully applied to the irradiation and modification of crystalline, polymer and nanostructures, such as carbon nanotubes. In this work the atomic-level processes involved in selective modification of oligomers for optoelectronic applications through thermal energy particle deposition are explored to identify the mechanisms by which different polyatomic ions and radicals assist in the stabilization of oligomer films. In particular, oligomer films of polythiophene are bombarded with incident H, CH_2 , C_2H and thiophene in the hyperthermal regime that involve incident energies of 4-50 eV. The results of classical molecular dynamics simulations with the REBO potential are compared to experimental findings, as well as linearly scaled density-functional theory molecular dynamics results. This work was supported by the NSF (CHE-0809376).

4:00pm SS1-MoA7 **Structure-Reactivity Relationships in the Electron Induced Reactions of Surface Bound Organometallics**, *H. Fairbrother*, *S. Rosenberg*, *J. Wnuk*, Johns Hopkins University, *C. Hagen*, *W. van Dorp*, *K. Landheer*, Delft University of Technology, Netherlands

Electron beam induced deposition (EBID) is a direct-write lithographic technique where volatile organometallic precursors are decomposed by a focused electron beam in a low vacuum environment to create metallic nanostructures. As a tool for nanofabrication, EBID offers an attractive and unique combination of capabilities including high spatial resolution and the flexibility to deposit free-standing three-dimensional structures without the need for resist layers. However, a major limitation of EBID is that nanostructures deposited from organometallic precursors typically possess unacceptable levels of organic contamination. To overcome this limitation it is crucial to develop a more detailed and fundamental understanding of how adsorbed organometallics undergo electron stimulated decomposition. Using a selected suite of organometallic precursors used in EBID ($\text{CH}_3\text{CpPt}(\text{CH}_3)_3$), $\text{Pt}(\text{PF}_3)_4$ and $\text{W}(\text{CO})_6$) I will describe how a surface science approach has been used to provide mechanistic and kinetic insights into EBID and to identify key structure-reactivity relationships. Central to our findings is the observation that for many organometallic precursors, EBID is initiated by the cleavage of a single metal-ligand bond and the release of the free ligand into the gas phase. However, subsequent electron stimulated reactions are characterized by decomposition rather than desorption of the residual ligands. Rationale design criteria for new organometallics which will decompose to produce metallic nanostructures with greater metallic purity have also been developed, such as the need to avoid using cyclopentadienyl ligands. In related studies we have also identified and rationalized the often significant effect that substrate temperature exerts on the composition of EBID materials created from organometallic precursors. Specifically, increased purity is expected for EBID films deposited at high substrate temperatures and low electron fluxes; the same conditions that reduce growth rates.

4:20pm SS1-MoA8 **Role of Substituents in Reactivity of Isocyanates Pre-Adsorbed on Ge(100)-2 \times 1**, *K.T. Wong*, *S.F. Bent*, Stanford University
Direct attachment of organic molecules to semiconductor surfaces offers the ability precisely control interfacial properties through tailoring of the organic molecule. This study focuses specifically on organic functionalization of germanium, as the ability to control its interfacial properties may enable devices to take advantage of its favorable electronic properties, as compared to silicon. Past studies have shown that a number of

isocyanate-containing molecules react with the Ge(100)-2×1 surface in ultra-high vacuum by [2+2] cycloaddition across the C=N bond of the isocyanate. In this study, we use *in situ* Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy to investigate further reaction following [2+2] cycloaddition. Density functional theory calculations are also used to corroborate and help understand these experimental results. We show that phenyl isocyanate pre-adsorbed on Ge(100)-2×1 is highly sensitive to subsequent exposure to water vapor. Experimental evidence suggests that water reacts with the adsorbed isocyanates to form a diphenyl urea compound, similar to what is expected for the reaction of phenyl isocyanate and water in solution. Extending the analogy with classic organic chemistry in solution, we find that addition of methyl or methoxy substituents to the phenyl ring of phenyl isocyanate can significantly decrease the adsorbed isocyanate's reactivity towards water. Such ability to easily tune the reactivity of an adsorbate-covered surface using principles from organic chemistry demonstrates the flexibility of organic functionalization and could be of importance when using organic functionalization for various applications.

4:40pm SSI-MoA9 Investigation of Adsorbed Sodium Dodecyl Sulfate Films Formed on Charged and Hydrophilic Surfaces. *S.-H. Song, T. Weidner*, National ESCA and Surface Analysis Center for Biomedical Problems, *M.S. Wagner*, The Procter & Gamble Company, *D.G. Castner*, National ESCA and Surface Analysis Center for Biomedical Problems

Surfactants are important compounds used in many industrial applications, with sodium dodecyl sulfate (SDS) being one of the most widely used surfactants. This study uses sum frequency generation (SFG) vibrational spectroscopy and surface plasmon resonance (SPR) sensing to investigate the structure of SDS films formed from the adsorption of SDS onto positively charged and hydrophilic surfaces. The surfaces studied included CaF₂ as well as RF glow discharge deposited films of allylamine. The SDS films were prepared by adsorption of SDS from water solutions ranging in concentration from 0.067 to 20 mM. Since the water molecules above the SDS layer interact with the films, peaks from both the SDS molecules and water molecules were studied. SFG spectra of SDS adsorbed onto the positively charged CaF₂ surface exhibits two well resolved CH₃ peaks at 2877 and 2942 cm⁻¹, and two OH peaks at ~3200 and ~3400 cm⁻¹. At the 0.2 mM SDS concentration on the CaF₂ surface the intensity of both the CH₃ and OH peaks decrease to close to background levels and then increase as the SDS concentration is raised. As the SDS solution concentration continues to increase the CH₃ and OH go through a second intensity minimum. This second intensity minimum occurs between 3-6 mM for the CH₃ peaks and near 8 mM for the OH peaks. Previous studies have suggested these SFG intensity minima are due to the neutralization of positively charged CaF₂ surfaces by the anionic charged head group of SDS (1). Since the shape and, thus, the phase of the SFG peaks are affected by the molecular environment, fits of the SFG data were used to quantify the orientation and alignment of the SDS layers across the wide range of SDS solution concentration. Since SFG is sensitive to both orientational order and the amount of material adsorbed we used SPR to determine the SDS coverage for the different solution concentrations in order to separate the two contributions. Combining SFG and SPR results provides a more detailed understanding of the structure and interactions of adsorbed SDS films.

(1) Becraft, K. A.; Moore, F. G.; Richmond, G. L. *Journal of Physical Chemistry B* **2003**, *107*, 3675.

5:00pm SSI-MoA10 Photon Stimulated Desorption of the Sub-Nanometer Size Clusters of Water, Methane, Ethylene, and Their Mixtures. *I. Arakawa, D. Matsumoto, S. Takekuma, R. Tamura, T. Miura*, Gakushuin University, Japan

Photon stimulated dynamics, such as desorption, dissociation, or chemical synthesis, at the water cluster which contains organic molecules have been studied in conjunction with the photochemistry at ice particles in cosmic space and in the atmosphere. In our experimental study, the clusters were prepared on the surface of a solid rare gas, which was condensed on the copper substrate cooled by liquid helium in an ultra high vacuum chamber. Our method has the advantage in controlling the cluster size and of high density of specimens in comparison with a molecular beam experiment. The clusters on the solid rare gas were excited by vacuum ultra-violet light with a photon energy between 12 and 108 eV with a pulse width of 10 ns, which was generated by a laser plasma light source [1]. The mass spectrum of photo-desorbed ions was measured by a time-of-flight (TOF) method. There are variety of species in the photo-desorbed ions from the co-adsorbed system of water and methane; protonated water clusters, (H₂O)_nH⁺, methane clusters, (CH₄)_nCH_k⁺, hetero-clusters of water and methane, (H₂O)_n(CH₄)_mCH_k⁺, and synthesized species, methanol, CH₃O⁺.

It was found that the presence of a water molecule in a cluster substantially enhanced, or was almost essential for, the desorption of any species, even for CH₃⁺ and CH₅⁺, observed in the spectrum. Dissociation of the water

molecule plays a key role in the chemical reaction in the clusters. It was also found that the desorption yield of each species showed strong dependence on the composition and the size of the mother cluster on the substrate, which were controlled by the amount of adsorption of water and methane. Close and systematic investigation of their correlation has revealed the mother cluster which yields the each desorbed ions: (H₂O)(CH₄) clusters yield CH₃⁺, CH₄⁺, (H₂O)CH₃⁺, and CH₃O⁺ while (H₂O)(CH₄)₂ clusters yield CH₅⁺, (H₂O)CH₃⁺, and C₂H₄⁺. These specific behaviors were also the case for the clusters of water and ethylene.

[1] T. Tachibana et al, *Surf. Sci.*, **593**, 264-268 (2005).

5:20pm SSI-MoA11 Nanobonding between 2-nm β-crystalalite SiO₂ on OH(1x1)Si(100) and SiO₂ for Monolithic Electronics by Surface Smoothing via Wet Chemical and Spin Processing: TMAFM Study and Modelling of Interphases. *S.D. Whaley*, ASU, *N.X. Herbots*, ASU / SiO₂ NanoTech Inc. / SiO₂ Associates, LLC, *J.D. Bradley*, SiO₂ Associates LLC / ASU, *R.J. Culbertson*, *M.A. Hart*, *D.A. Sell*, *Q.X. Bradley*, ASU, *R.L. Rhoades*, *S.N. Drews*, Entrepix, Inc., *R.B. Bennett-Kennett*, ASU

β-crystalalite nanofilms, 2-nm thick, are nucleated on OH(1x1)Si(100) via the Herbots-Atluri (H-A) method [1,2] and form ultra-smooth, ordered, interphases that desorb at low temperatures (T <~ 200 °C) [3] These ordered oxide nanophases on OH(1x1)-Si(100) promote oxidation at low temperatures in ambient, when in contact with oxygen-deficient phases of SiO₂ used in electronics. They can nucleate and grow a cross-bonding interphase between two substrates and achieve "nanobonding" [4] between various combinations Si and silica.

Nanobonding means forming cross-bonding molecules which condense into a continuous macroscopic bonding interphase between 2 smooth surfaces put into mechanical contact. For this to occur, the surfaces need to exhibit wide flat atomic terraces (width >/10 nm), low atomic step density (< 500 steps/μm across atomic terraces direction) and very low particulate density (less than 1/100 μm²). This contrasts with the typical density of surface steps (~ 500 steps/μm a.a.t.d.) and particulate density >/0.1 -1 μm² in as received wafers or post-processing. A surface step density ≥ 500 step/μm a.a.t.d, typically found on Si(100) with miscuts < 0.025° and particulates densities ≥ 0.1 μm⁻² particulates results in 3-dimensional isolated bonding points of contacts as opposed to more uniform, 2-dimensional interphases that grow laterally as well as across is shown to occur in nanobonding. Wet chemical processing and SEZ spin technology are compared and combined to smoothen substrates via the H-A chemistry [1,2] via Tapping Mode Atomic Force Microscopy, before and after nanobonding. Our results show nanobonding can result in bonding strength larger than 10 MPa/cm² as measured by mechanical bond pull tests. Wafers fracture within the bulk of both Si and silicate substrates rather than interfacial delamination.

[1] US Patent 6,613,677, issued 9/2/03 "Long range ordered semiconductor interface phase and oxides." 6,613,677, Herbots, N.; Atluri, V. P.; Bradley J.D.; Swati, Banerjee; Hurst, Q.B.; Xiang, J.

[2] US patent 7,851,365 issued 12/14/10, "Methods for preparing semiconductor substrates & interfacial oxides there on" Herbots N., Bradley J.D., Shaw J.M., Culbertson and Atluri V.P.

[3] Patent Filed: 4/30/09, "Low Temperature Wafer Bonding and for Nucleating Bonding Nanophases. N. Herbots, R. J. Culbertson, J.D. Bradley, M. A. Hart, D. A. Sell and S. D. Whaley

[4] N. Herbots, Q. Xing, M. Hart, J. D. Bradley, D. A. Sell, R. J. Culbertson, Barry J. Wilkens; "IBMM of OH Adsorbates and Interphases on Si-based Materials". *Nucl. Instr. and Meth. in Phys. Res.*, B. IBMM 17th International Conference Proceeds (Aug, 2010), accepted

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