

Monday Morning, November 9, 2009

Surface Science

Room: M - Session SS1-MoM

Vibrational Spectroscopy and Surface Reactions

Moderator: Y. Chabal, University of Texas, Dallas

8:20am **SS1-MoM1 Reaction of Phenylenediamines on Ge(100)-2x1: The Effects of Functional Group Spacing on Reactivity.** *J.S. Kachian, K.H. Squires, S.F. Bent*, Stanford University

While silicon is the current material of choice in the electronics industry, next-generation device requirements make the largely unexplored surface chemistry on germanium, a Group IV homolog with promising electrical properties, an interesting area of study. Multifunctional adsorbates are of particular interest, since they inherently offer a greater degree of tailorability and the potential for subsequent reaction. The adsorption of the *o*-, *m*- and *p*- structural isomers of phenylenediamine on Ge(100)-2x1 at room temperature was investigated to gain a fundamental understanding of how surface bonding of these molecules is affected by the distance between two NH₂ groups attached to a rigid benzene ring. Vibrational spectra of the adsorption products of these three molecules, obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy in ultrahigh vacuum (UHV), show that all three isomers adsorb via N-H dissociation. The corresponding X-ray Photoelectron Spectroscopy (XPS) results support the MIR-FTIR data and further reveal the bonding configurations of the N-H dissociated adducts at the surface: While there is evidence of both singly and dually N-H dissociated adducts for the ortho isomer, N-H dissociation of only one amino group is observed for the para isomer, while N-H dissociation of both amino groups is observed for the meta adducts. Dative bonding was not observed for reaction of any of the phenylenediamine isomers with the Ge(100)-2x1 surface. The difference in reactivity between isomers likely results from how closely the spacing between NH₂ groups on the benzene ring matches the distance between adjacent surface dimers. The distance is in closest agreement for the meta isomer, which adsorbs exclusively via dual N-H dissociation, and is most mismatched for the para isomer, which adsorbs only via single N-H dissociation. Adsorption of the ortho isomer, which represents an intermediate case geometrically, leads to a mixture of singly and dually N-H dissociated adducts. DFT calculations support the experimental results. The results will be compared to those obtained for reaction of aniline, the monofunctional analog to the phenylenediamine isomers, on Ge(100)-2x1.

8:40am **SS1-MoM2 Electronic and Steric Effects in the Reactions of Isocyanates and Isothiocyanates at the Ge(100)-2x1 Surface.** *P.W. Loscutoff, K.T. Wong, S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces has seen increased interest in recent years, due to the ever-decreasing feature sizes of microelectronics, and the advance of organic electronics. Advances in both of these fields require precise interface control at atomic dimensions, and modification of surfaces with organic molecules provides the flexibility necessary for use in a broad spectrum of applications. In this study, we examine the surface products formed by the reactions of various isocyanates and isothiocyanates with the Ge(100)-2x1 surface. Although these two moieties differ only by substitution of an oxygen atom with a sulfur atom, they display markedly different reactivity at the reconstructed germanium surface. Using a combination of infrared spectroscopy, x-ray photoelectron spectroscopy and density functional theory, we examine the reactions of phenyl, *tert*-butyl, and ethyl isocyanate and the corresponding isothiocyanates. Both phenyl isocyanate and phenyl isothiocyanate form multiple adsorption products at the surface. The isocyanate reacts with a Ge surface dimer to form a [2+2] cycloaddition product across the C=N bond to produce a surface-bound carbonyl in addition to other products. In contrast, phenyl isothiocyanate reacts across the C=S bond to form a [2+2] cycloaddition product, in addition to reaction across the C=N bond. When the *tert*-butyl group is substituted for the phenyl ring, the reactivity changes such that dative-bonded products with an intact, surface-bound isocyanate or isothiocyanate group are observed. Upon reaction of ethyl isocyanate and ethyl isothiocyanate at the Ge(100)-2x1 surface, yet another product distribution is observed, which lacks dative-bonded products but demonstrates time-dependence. The wide array of products observed for this set of isocyanate and isothiocyanate molecules demonstrates the influence of the molecular chain on the surface reactivity of these groups, and displays a versatility that could prove useful for tuning reactivity to achieve a desired surface product.

9:00am **SS1-MoM3 Surface Transamination Reactions for Thin Film Deposition on NH_x-Precovered Silicon.** *A.V. Teplyakov*, University of Delaware **INVITED**

The termination of semiconductor surfaces plays a major role in surface reactivity and in our ability to create a well defined and sharp interface between a semiconductor and a thin film, often required for practical applications. Although hydrogen termination of group IV semiconductors is often a good starting point for deposition chemistry, the reactivity of hydrogen terminated surfaces is often limited. Here we selectively produce a specific NH_x termination of Si(100) surface by exposing it to ammonia and briefly annealing at a predetermined temperature. The reactivity of silicon surfaces prepared in such a way is examined by reacting them with a common organometallic precursor for thin diffusion barrier film growth, tetrakis(dimethylamido)titanium, TDMAT. Experimental observations suggest the occurrence of a surface transamination reaction, where an approaching TDMAT molecule reacts with a surface NH_x site, eliminating dimethylamine and attaching Ti to the surface N atom. Vibrational spectroscopy holds the key to determining this reactivity and surface reaction pathways. Together with temperature programmed desorption and computational DFT investigations, these studies expand the generality of transamination processes to other amines on Si(100). The role of steric and electronic factors is evaluated for improving proposed deposition schemes.

9:40am **SS1-MoM5 Si ALE using Molecular Disilane on Si(100)-(2x1).** *I.S. Chopra, J.-F. Veyan, M.P. Nadesalingam, N. Dao, O. Seitz, W.P. Kirk*, The University of Texas at Dallas, *J. Randall, Zyvex Labs, M. Huang, K. Cho, R.M. Wallace, Y. Chabal*, The University of Texas at Dallas

Atomic layer epitaxy (ALE) is a critical step in trying to achieve Atomically Precise Manufacturing (APM) of new devices such as quantum dots, qubits, NEMS oscillators and biomedical devices. Here we report the ALE of Si using molecular disilane on (2x1)-Si(100) surface. The surfaces have been characterized using Fourier transform infrared spectroscopy (FTIR), angle resolved x-ray photoelectron spectroscopy (ARXPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS).

IR absorption measurements have been performed in transmission mode (70° incidence). Clean Si(100)x(2x1) samples are prepared by controlled thermal desorption of chemically oxidized Si wafers. On clean (2x1) – Si(100) surfaces, saturation doses of the order of 10L are observed, which is considerably lower than data reported earlier (3000L)¹. At saturation coverage absorption bands in the ~2100 cm⁻¹ range (and also ~950 and 650 cm⁻¹) indicate that monohydrides (SiH), dihydrides (SiH₂) and trihydrides are formed, consistent with shifts of the Si2p core level using angle resolved X-ray photoelectron spectroscopy. The relative intensities of these bands have been studied as a function of exposure and substrate temperature, and present differences from earlier room temperature measurements.² The observation of trihydrides indicates that one product from disilane decomposition is the silyl group, although its concentration depends on exposure and temperature. The thermal stability of these resulting surfaces has been examined with infrared absorption, temperature-programmed desorption (TPD) and LEED. We have also examined the effects of He ion surface de-passivation.³

To gain a fundamental understanding on surface reaction mechanisms, we have performed a density functional theory (DFT) study on the reactions of monohydrides (SiH), dihydrides (SiH₂), trihydrides and disilane on both clean and hydrogen passivated Si(100)-(2x1) surfaces. The calculated atomic configurations, electronic structures, and vibration frequencies are compared with the experimental data.

References

- 1 Yoshiyuki Suda, Naoyuki Hosoya and Kazushi Miki, *Appl. Surf. Sci.* 216, 424-430 (2003).
- 2 Masanori Shinohara, Michio Niwano, Yoichiro Neo and Kuniyoshi Yokoo, *Thin. Solid Films* 309, 16-20 (2000).
- 3 This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:00am **SS1-MoM6 Adsorption Studies of Molecular Disilane on p-type Ge(100) at Room Temperature.** *M.P. Nadesalingam, N. Dao, I.S. Chopra, J.-F. Veyan, W.P. Kirk*, University of Texas at Dallas, *J. Randall, Zyvex Labs, Y. Chabal, R.M. Wallace*, University of Texas at Dallas
ALE (Atomic Layer Epitaxy) is a layer by layer epitaxial thin film growth technique of interest for fabrication of SiGe high speed devices¹ as well as

enabling atomically precise manufacturing (APM) of nanometer scale features. We report on a precision gas dosing technique for Si ALE on Ge(100) p-type using molecular disilane.

The adsorption of molecular disilane on Ge(100) was studied using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS) and Fourier transform infrared spectroscopy (FTIR). LEED analysis shows that the Ge surface periodicity results in a weak 2x1 pattern upon exposure to molecular disilane. The molecular disilane was delivered to the Ge(100) substrate using micro-capillary array molecular beam doser with an equivalent dose of ~1.2 L, which is a considerably smaller value compared to that reported from previous techniques.² Based on the XPS data, the Si coverage on Ge is nearly half a monolayer.³ The sticking coefficient of molecular disilane on Ge (100) is estimated to be 0.48 with disilane adsorption on Ge(100) that is governed by dissociating Si₂H₆ into two silyl(-SiH₃) groups. IR absorption measurements have been performed in transmission mode (70° incidence) to analyze the adsorption mechanisms as a function of temperature and coverage.⁴

References

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3. D. S. Lin, T. Miller and T. C. Chiang, Phys. Rev. **B 47**, 6543 (1992).
4. This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:40am **SS1-MoM8 High-stability Molecular Interfaces to TiO₂ Surfaces**, *R. Franking, H. Kim, E.C. Landis*, University of Wisconsin, Madison, *S.A. Chambers*, Pacific Northwest National Laboratory, *R.J. Hamers*, University of Wisconsin, Madison

The integration of molecular systems with TiO₂ is of interest in a wide range of emerging applications; however, most methods currently used are not stable under in aqueous media, especially at elevated temperatures or extremes of pH. We demonstrate that well-defined molecular layers can be covalently bound to the surface of nanocrystalline and single-crystal anatase TiO₂ by photochemically grafting organic molecules bearing a terminal vinyl group. Stability tests on nanocrystalline films show the layers have excellent stability in aqueous environments with a wide range of pH for time scales approaching 2 months, and that grafting occurs through the thickness of 10 micron thick porous films. XPS, FTIR, and wavelength-dependent excitation experiments have been performed to help identify the reaction pathway. New methods are being developed using the highly stable chemistry to create highly flexible, modular interfaces with the oxide.

11:00am **SS1-MoM9 HREELS Study on the Doping of ZnO by H and Cu Atoms**, *H. Qiu, Y. Wang, Ch. Wöll*, Ruhr-University Bochum, Germany Zinc oxide exhibits a number of extraordinary properties and is one of the most technologically important metal oxides [1]. Presently, there is great interest in the doping of ZnO by foreign atoms due to its effects on changing the electrical, optical and catalytic properties of ZnO. In this contribution, the interaction of hydrogen and Copper atoms with ZnO(000-1) was studied by high resolution electron energy loss spectroscopy (HREELS) which recently has been successfully applied to perfect and defective metal oxide surfaces [2].

Exposing the fully hydroxylated ZnO(000-1) surface to atomic hydrogen leads to a significant broadening of the quasi-elastic peak in HREELS, which corresponds to the existence of free charge carriers at ZnO surface region [3]. These free charge carriers result from the thermal excitation of electrons at the donor level into the conduction band. The shallow donor states are created via diffusion of H atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 25 ± 5 meV [4].

Cu deposition on O-ZnO leads to the formation of well-defined islands with the Cu(111) facets. For the small clusters the partial oxidation of Cu⁰ into Cu⁺ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the bulk. The doping of ZnO by Cu leads also to the formation of shallow donor states, in which the electrons can be thermally excited into the conduction band and, as a result, giving rise to the plasmon-induced broadening of the quasielastic peak in HREELS. From the observed temperature dependence, the donor level ionization energy was determined. This unexpected doping effect of ZnO by Cu has important consequences

for its chemical activity, as confirmed by the detailed studies on CO₂ adsorption.

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11:20am **SS1-MoM10 Reactions of NO₂ with BaO and Ba(OH)₂ on Pt(111)**, *K. Mudiyansele*, Pacific Northwest National Laboratory, *C.W. Yi*, Sungshin Women's University, Korea, *J. Szanyi*, Pacific Northwest National Laboratory

Reactions of NO₂ (in the pressure range of 1.0 × 10⁻⁹ - 1.0 × 10⁻⁴ Torr) with BaO(> 20 MLE), amorphous-Ba(OH)₂ and crystalline-Ba(OH)₂ supported on Pt(111) were studied using infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The amorphous and crystalline Ba(OH)₂ layers were prepared by adsorbing H₂O on BaO(> 20 MLE)/Pt(111) at 300 and 425 K, respectively. The amorphous-Ba(OH)₂ layer partially converts to Ba(NO_x)₂ (nitrites and nitrates) following exposure to elevated NO₂ pressure (~1.0 × 10⁻⁴ Torr) at 300 K. The exposure of the crystalline-Ba(OH)₂/Pt(111) system to NO₂ at 425 K leads to the desorption of H₂O and the complete conversion of the crystalline-Ba(OH)₂ layer to Ba(NO_x)₂, which consists of mainly crystalline nitrates and a small amount of nitrites. Adsorption of NO₂ on BaO(> 20 MLE)/Pt(111) at 425 K also forms crystalline nitrates. The amounts of NO_x uptaken by BaO(> 20 MLE)/Pt(111) and crystalline-Ba(OH)₂/Pt(111) systems at 425 K are very similar as determined by the NO TPD peak areas.

11:40am **SS1-MoM11 In-situ Spectroscopy Studies of Surface Species on Pd Surfaces during CO Oxidation**, *M.S. Chen, X. Wang, H.L. Wan*, Xiamen University, China

Previous we had found that CO oxidation on Pd-group metals at temperatures between 450 and 600 K and pressures between 1 and 300 Torr increases markedly with an increase in the O₂/CO ratio above 0.5. [Surf. Sci. **2007**, **601**, 5326.] The catalytic surfaces, formed at discrete O₂/CO ratios > 0.5, exhibit rates 2 to 3 orders of magnitude greater than those rates observed for stoichiometric reaction conditions and similar reactant pressures or previously in ultrahigh vacuum studies at any reactant conditions and extrapolate to the collision limit of CO in the absence of mass transfer limitations. Here we used HREELS to address the relative activities of surface CO and oxygen species. The surface oxygen species can be removed by CO at room temperature and low pressure, 10⁻⁸ Torr. While a much higher oxygen pressure or above room temperature is required to remove surface adsorbed CO species. Furthermore, *in-situ* RAIRS and Raman spectroscopy were used to characterize this highly active surface formed at higher O₂/CO ratios on Pd.

Keywords: CO oxidation, Pt-group metal, Oxygen covered surface

Surface Science

Room: N - Session SS2-MoM

TiO₂ Surfaces and Interfaces

Moderator: D.A. Chen, University of South Carolina

8:20am **SS2-MoM1 Surface Structures of TiO_x Thin Films on Au (111)**, *C. Wu, M.R. Castell*, Oxford University, UK

Well-ordered ultrathin titanium oxide layers were grown on reconstructed Au (111) surfaces by Ti evaporation at room temperature and post-deposition oxidation at a pressure of 10-6 Pa O₂ and a temperature of around 600 °C. Depending on the amount of Ti deposited, three different structures were observed. The structures were characterized by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

With Ti coverage below one monolayer (ML), an epitaxial oxide honeycomb structure is created. The herringbone reconstruction of the Au (111) substrate is lifted underneath the titanium oxide monolayer. STM

reveals that the contrast between the honeycomb monolayer and the gold reconstruction is influenced by both tip termination and imaging bias. The measured periodicity and crystallographic alignment of the honeycomb structure indicates a (2×2) reconstruction on Au (111). XPS and AES data show the deposited titanium is fully oxidized to TiO₂. Increasing the Ti dose up to 2 MLs gives rise to a pinwheel structure that coexists with the honeycomb on the surface. The spokes of the pinwheels are parallel to the three close-packed directions of the honeycomb structure. Triangular islands start to grow and coalesce with higher Ti coverage. It is difficult to resolve the structure on the islands, but after 1.5 hours annealing of the thicker films, a row-like structure can be observed with a periodicity of 0.95 nm across the rows. XPS and AES indicate the presence of the Ti²⁺ oxidation state.

8:40am **SS2-MoM2 Geometric Structure of the TiO₂(011) (2x1) Surface by Low Energy Electron Diffraction (LEED)**, *S.E. Chamberlin, H.C. Poon, D.K. Saldin, C.J. Hirschmugl*, University of Wisconsin - Milwaukee

The surface of TiO₂ has been extensively studied to explore its potential for many applications, including the harvesting of solar light and the photocatalysis of water [1-3]. The majority of studies have focused on the thermodynamically most stable rutile (110) face [4], however, other faces are almost as important. For example, the rutile (011) face may have enhanced activity towards water dissociation [5], but is less studied. Crucial to understanding the mechanisms by which these processes occur is determining the atomic structure and chemistry of the surface.

The (011) surface of TiO₂ is known to exhibit a (2x1) reconstruction [6] and several models of the surface have been proposed [6-9]. The present work extends quantitative low energy electron diffraction (LEED) to reconstructed oxide surfaces in order to determine which, if any, of these models are supported by LEED-IV. I-V curves, with a total energy range of ~2200 eV, were extracted for 20 beams using a novel, low-current, delay-line-detector LEED (DLD-LEED) system to minimize effects due to charging and electron beam damage. Structural refinement from the LEED-IV analysis confirms the Brookite model [8] found by surface x-ray diffraction, with agreements in atomic displacements to within 0.04 Å perpendicular to the surface and 0.12 Å parallel to the surface. The resulting Pendry R-factor is 0.29 which definitively excludes the other proposed models that give significantly higher R factors.

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9:00am **SS2-MoM3 Metal Oxide Surfaces: Defects, Dopants, and Reactivity**, *U. Diebold*, Tulane University **INVITED**

Metal oxides are versatile materials and are used in a wide variety of technical fields. In many applications, surface properties play a critical role in device functioning. Our group is investigating the atomic-scale properties of metal oxide surfaces with Scanning Tunneling Microscopy (STM) and area-averaging surface spectroscopies. DFT calculations, conducted in collaboration with theoretical groups, are instrumental in data analysis and interpretation.

In the talk we report recent results on metal oxide materials that have industrial relevance but are rarely studied with surface science techniques. We find that on a TiO₂ anatase (101) surface standard preparation procedures lead to *sub*surface rather than surface oxygen vacancies [1]. Adsorbed water shows an interesting short-range ordering that is governed by substrate-mediated repulsive/attractive interactions [2]. The surface structure of epitaxial films of Sn-doped In₂O₃ (ITO) is discussed [3].

- [1] Y. He *et al.*, *Phys. Rev. Lett.* **102**, 106105 (2009).
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9:40am **SS2-MoM5 Controlled Manipulation of Oxygen Vacancies on TiO₂(110)-1x1 Using LT-STM**, *D. Acharya, P.W. Sutter*, Brookhaven National Laboratory

Titanium dioxide (TiO₂) – widely used in, photocatalysis, heterogeneous catalysis, gas sensors, and solar cells – has become the prototype material for studying the chemical reactivity of metal oxide surfaces. Oxygen vacancies are among the primary chemically active defects on this surface, as well as on other reducible transition metal oxides. We report the controlled manipulation of individual O-vacancies (Ov) on reduced TiO₂(110)-1x1 in low temperature scanning tunneling microscopy. Using localized voltage pulses, the hopping of oxygen vacancies can be controlled precisely along the bridging oxygen rows. We apply this single-vacancy manipulation to study the interaction of closely spaced vacancies, and to establish the possibility of forming highly reactive double and triple Ov clusters. The occurrence of such defects with exposed low-coordinated Ti atoms has implications on the reactivity of TiO₂(110) and of similar metal-oxide surfaces.

10:00am **SS2-MoM6 Oxygen Reactivity on Reduced TiO₂(110)**, *N.G. Petrik, G.A. Kimmel*, Pacific Northwest National Laboratory

The interaction of oxygen with TiO₂ is critical for a variety of applications including the photooxidation of organic materials, purification of water and air, and (potentially) photocatalytic water splitting. In this paper, the thermal and non-thermal (photon- and electron-stimulated) reactions of molecular oxygen are studied versus oxygen coverage on reduced TiO₂(110). At low temperatures, two O₂ can chemisorb per oxygen vacancy (V_O).¹ Hydroxylation of the vacancies (via dissociative water adsorption) does not affect the amount of chemisorbed O₂. Most of the chemisorbed molecules do not desorb upon annealing to 700 K, but react. The thermal reactions of the chemisorbed O₂ depend strongly on the oxygen coverage. When 1 O₂ is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~200 K, healing the vacancy and depositing an oxygen adatom on the Ti row. At an oxygen coverage of 2 O₂ per oxygen vacancy, the oxygen converts to another species (perhaps tetraoxygen or ozonide) in temperature range of 200 K < T < 400 K. This species subsequently decomposes at higher temperatures. The photon- (and electron-) stimulated desorption of chemisorbed oxygen are also very sensitive to the oxygen coverage. The results demonstrate that the reactivity of TiO₂(110) with O₂ is primarily controlled by the amount of electron-donating surface species on the surface (V_O's and/or hydroxyls).²

¹ G.A. Kimmel and N.G. Petrik, *Phys. Rev. Lett.* **100**, 196102 (2008).

² N.G. Petrik, Z. Zhang, Y. Du, Z. Dohnalek, I. Lyubinetzky, G.A. Kimmel, *JCP submitted*

10:40am **SS2-MoM8 Oxygen Interactions with Hydroxylated TiO₂(110) Surfaces**, *Y. Du, A. Deskins, Z. Zhang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M. Dupuis, I. Lyubinetzky*, Pacific Northwest National Laboratory

Reactions leading from O₂ to H₂O on catalytically active surfaces often involve intricate mechanisms with a number of possible surface-bond intermediates, such as OH, HO₂, or H₂O₂. Such reactions on surfaces are challenging to explore with ensemble-average techniques because of the extremely small number of participating molecules and the difficulty in resolving intermediates spectroscopically.

In this work, the reaction of O₂ with both partially and fully hydroxylated TiO₂(110) surface was directly followed by STM. The consecutive steps of both primary and secondary site-specific reactions have been tracked by comparing the atomically resolved STM images of same surface area before and after O₂ exposure. As a result, we have directly imaged two chemical intermediates, terminal OH and OOH, which have been proposed to play key roles in the interconversion of oxygen and water. By combining the site-specific STM and ensemble-averaging TPD/ESD studies, we also find that H₂O can participate in the reaction process in multiple ways – as a reactant, product, and catalyst. Specifically, water mediates the diffusion of surface species that would otherwise be stationary, and thus brings reactants together, catalyzing the reactions with O₂. As a result, most of the OH_b's can be removed via reaction with O₂ such that a fully hydroxylated surface can be converted to a nearly stoichiometric surface.

11:00am **SS2-MoM9 The Photochemistry of Trifluoroacetone on TiO₂(110)**, *R.T. Zehr, M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced photodecomposition of 1,1,1-trifluoroacetone (TFA) adsorbed on the rutile TiO₂(110) surface has been investigated with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). TFA adsorbed on the reduced surface (8% oxygen vacancies) showed a molecular desorption peak at 260 K that shifts to 220 K with increasing TFA coverage, indicative of inter-adsorbate repulsion in the adsorbed layer. Adsorption of TFA on a reduced TiO₂

surface pre-exposed to 20 L O₂ leads to the formation of a TFA peak at 350 K accounting for 2/3rd ML coverage. A second peak at 250 K (1/3rd ML) completes the monolayer. Irradiation of the TFA covered oxidized surface by UV light at 90 K reduces the intensity of the 350 K TPD peak, with the 250 K state unaffected. Post-irradiation TPD shows evidence of the formation of small amounts of acetate (evolving as ketene at 650 K) as a surface bound decomposition product. UV irradiation of TFA causes the near complete photodecomposition of the photoactive species, leading to PSD of CH₃, CF₃, and CO during irradiation. This result is in contrast to the photochemical behavior of acetone, butanone and acetaldehyde on TiO₂(110), where the gas phase ejection of only one of the two carbonyl substituent groups is observed and a stoichiometric amount of carboxylate is left on the surface. We conclude that fluorination alters the electronic structure of adsorbed carbonyls on TiO₂(110) in such a way as to promote complete fragmentation of the adsorbed carbonyl complex.

(This work was supported by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences and performed in the Environmental Molecular Sciences Laboratory at PNNL.)

11:20am **SS2-MoM10 TiO₂ with Subsurface Metallic Nanoclusters for Stimulating Photochemistry**, *F. Womack, F. Wang, Z. Zhang, P. Sprunger, R.L. Kurtz*, Louisiana State University

Metallic nanoclusters can be buried within nanometers of the surface of TiO₂ and can enhance photoabsorption to produce hot electron-hole pairs for surface chemistry. When Ag is grown on TiO₂(110), STM shows that it forms ~ 5nm clusters, and HREELS shows a plasmon resonance at 3.7 eV. AFM shows that these clusters remain after coating with a thin layer of titania and conducting probe AFM shows that the conductivity in the vicinity of the clusters is enhanced consistent with their metallic nature and increased defect densities in the oxide. HREELS shows that the plasmon resonance of the nanocluster is red-shifted and broadened to 1.5-2 eV when encapsulated in titania and these findings are supported by optical measurements. The nanoclusters induce defects within the surrounding titania and the role that Ti³⁺ defects, O-vacancies, and Ti-interstitials play in Ag/TiO₂ interactions as probed with synchrotron-based photoemission will be discussed. Electrochemical measurements have been conducted to test photochemical performance in electrolyte, and subsequent surface analysis provides information on the changes induced in morphology, defect densities, and oxidation states.

We acknowledge the support of NSF through CHE-0615606.

11:40am **SS2-MoM11 Switching of Sulfur Lattice Sites in S-doped TiO₂(110) Under Controlled Annealing Environments**, *N. Athavan, Portland State University, V. Shutthanandan, P. Nachimuthu, S. Thevuthasan*, Pacific Northwest National Laboratory

TiO₂ is one of the most heavily studied materials for photocatalytic water splitting even though it has a poor overlap of its optical absorption spectrum with the solar spectrum and high e⁻/h⁺ pair recombination rate. Band gap reduction is one approach to enhance visible light absorption in TiO₂. Anion (N, C and S) doping causes a red shift of the absorption edge into the visible region and visible-light-induced photochemistry has been observed on these materials. Recently, we have investigated S doped TiO₂(110) rutile by ion implantation as a function of substrate temperatures and dopant concentrations. Subsequently high-temperature annealing was carried out on selected samples to heal the implantation damage as well as to understand the location and mobility of the dopants in the rutile lattice. Following implantation and annealing, the samples were characterized using several surface and bulk sensitive techniques such as x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and proton induced x-ray emission (PIXE) in both random and channeling directions. Depth profile of S implanted TiO₂ was obtained using XPS. PIXE was used to locate the lattice sites of S while NRA and RBS were used to measure the lattice sites of oxygen and titanium atoms, respectively. PIXE measurements along the channeling and random geometries clearly demonstrate the substitution of sulfur for oxygen in TiO₂ lattice under certain implantation conditions. Angular scans obtained around <110> were used to investigate the lattice site locations of sulfur at different annealing conditions. When the implanted sample is further annealed at 700°C for 1 hour at 100 Torr of oxygen, the sulfur atoms moved from the substitutional sites to interstitial sites. Subsequent annealing in vacuum (1 x10⁻⁵ Torr) at 800°C for 1 hour showed that the displaced sulfur atoms reoccupied the substitutional sites. Additional vacuum annealing at 900°C is not only retained the S atoms at the oxygen lattice sites but also improved the overall crystalline quality of the implanted region.

This work is supported by grants from DOE BES Division of Chemical Sciences and Office of Biological and Environmental Research

Graphene Topical Conference

Room: C3 - Session GR+SS-MoA

Epitaxial Graphene on SiC

Moderator: P.N. First, Georgia Institute of Technology

2:00pm **GR+SS-MoA1 Observing the Quantization of Zero Mass Carriers in Epitaxial Graphene, J.A. Stroschio**, National Institute of Standards and Technology **INVITED**

The cyclotron motion of electrons in a magnetic field has historically been a powerful probe of the Fermi surface properties of metals and two-dimensional electron systems. Oscillations in many measurable properties such as magnetization, thermal conductivity, and resistance, all reflect the quantization of closed orbits and the resulting discrete density of states due to the formation of Landau levels. Here, we show a new ability to observe magneto-oscillations in scanning tunneling spectroscopy of epitaxial graphene as a function of both magnetic field and electron energy [1]. These oscillations arise from Landau quantization of the 2-dimensional Dirac electron and hole quasiparticles in the topmost layer of multilayer epitaxial graphene grown on SiC. In normal metals and two dimensional electron gases the Landau levels are equally spaced. In graphene however, the charge carrier velocity is independent of their energy. Consequently, the Landau level energies are not equally spaced and include a new characteristic zero energy state (the $n=0$ Landau level). Using scanning tunneling spectroscopy of graphene grown on silicon carbide, we directly observe non-equally spaced energy level spectrum of Landau levels, including the hallmark zero-energy state of graphene. We measure the local variation in the electrostatic potential of graphene by spatially mapping the $n=0$ Landau level. As the magnetic field is varied at fixed tunneling energy, oscillations are detected in the tunneling conductance, which are shown to be a method to measure low energy electronic band structure. These tunneling magneto-conductance oscillations are used to determine the linear energy-momentum dispersion of graphene through the Dirac point with extremely high energy and momentum resolution.

[1] David L. Miller, Kevin D. Kubista, Gregory M. Rutter, Ming Ruan, Walt A. de Heer, Phillip N. First, Joseph A. Stroschio, Science (in press).

2:40pm **GR+SS-MoA3 Graphene Materials Development, G.G. Jernigan, J.L. Tedesco, J.G. Tischler, E. Glaser, J. Caldwell, P.M. Campbell, D.K. Gaskill**, US Naval Research Laboratory, **J.A. Robinson, M.A. Fanton**, Electro-Optics Center Penn State

Development of graphene is a materials issue. Exfoliated graphene has shown the promise of high carrier mobilities, but for graphene to become technologically viable, epitaxial graphene formed over large areas must be developed. Reported carrier mobilities for epitaxial graphene grown on SiC range from $> 250,000$ to $< 1,000$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Mobility results can vary with measurement method, measurement temperature, and sample size. We will present our results, which encompass the aforementioned range of mobilities, for graphene formed on Si-face and C-face SiC.

Utilizing semi-insulating substrates, we have been able to correlate electrical characteristics with materials properties, which are dependent on the surface termination of SiC. Si-face graphene consistently shows lower mobilities than graphene grown on the C-face. XPS shows the differences between growth on the Si-face and the C-face are 1) the presence of an interfacial layer between the graphene and the SiC for Si-face films and 2) electronic differences between the C 1s peak for graphene on the C-face and the C 1s peak for graphene on the Si-face. The electronic differences may result from more graphene layers form on the C-face than on the Si-face. In particular, graphene forms only 1 to 3 layers on the Si-face even for long growth times at high temperature (e.g. 60 min at 1600 °C). STM images of graphene on the Si-face show an islanding mode of growth, which leads to the development of grain boundaries within the film, and μ -Raman measurements show that the mobility increases as the domain size increases. Graphene formed on the C-face of SiC grows very rapidly, leading to films which are 10 to 30 nm thick and decorated with striped surface features (referred to as "giraffe stripes"). Independent of the presence of giraffe stripes, we observe that surface roughness does affect mobility, with smoother surfaces having higher mobilities. We have also performed far infrared magneto-transmission measurements (FIR-MT) on the graphene films. The C-face graphene shows a $0(-1) \rightarrow 1(0)$ Landau level transition with a \sqrt{B} dependence and linewidths consistent with layers having carriers described as Dirac fermions with mobilities $> 250,000$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at 4.2K. The Si-face graphene showed much broader linewidths resulting from lower carrier mobility. One trend that holds for graphene on both faces of SiC is that fabrication of small area devices can result in

higher carrier mobilities and that carrier mobility increases as the carrier density decreases. Continued improvements in the electrical characteristics of epitaxial graphene can be realized through improvements in material quality.

3:00pm **GR+SS-MoA4 Defects Scattering in Graphene, J.-H. Chen, W. Cullen, C. Jang, M. Fuhrer, E. Williams**, University of Maryland, College Park

We have measured the effect of low energy charged particle irradiation on the electronic transport properties of clean graphene devices. Irradiation of graphene by 500 eV Ne and He ions creates defects that cause intervalley scattering as evident from a significant Raman D band intensity. The defect scattering gives a conductivity proportional to charge carrier density, with mobility decreasing as the inverse of the ion dose. The mobility decrease is four times larger than for a similar concentration of singly charged impurities. The minimum conductivity decreases proportional to the mobility to values lower than $4e^2/\pi h$, the minimum theoretical value for graphene free of intervalley scattering. Defected graphene shows a diverging resistivity at low temperature, indicating insulating behavior. The results are best explained by ion-induced formation of lattice defects that result in mid-gap states.

3:40pm **GR+SS-MoA6 Formation of Epitaxial Graphene on SiC{0001}; Comparison of Si-face and C-face, P. Fisher, IBM, L. Luxmi, N. Srivastava, R. Feenstra**, Carnegie Mellon University, **Y. Sun**, Argonne National Laboratory, **J. Kedzierski**, MIT Lincoln Laboratory

The formation of epitaxial graphene on the SiC{0001} surface is described, comparing results for (0001) and (000 $\bar{1}$) surfaces (the so-called *Si-face* and *C-face*, respectively). The graphene is formed by heating the SiC to 1100 – 1400°C for 20 min in vacuum, during which time the Si preferentially sublimates, leaving behind the C which self-assembles into graphene. Development of the graphene layer(s) is observed by atomic force microscopy (AFM), low-energy electron diffraction and Raman spectroscopy, with the graphene thickness measured using both Auger electron spectroscopy and low-energy electron microscopy. High quality films are formed, with field-effect mobilities at room temperature exceeding 4000 cm^2/Vs . It is found that graphene forms as 3-dimensional islands on the C-face, whereas it forms in a 2-dimensional manner on the Si-face. We believe that this difference occurs because of differing interface structures between the graphene and the SiC in the two cases. Importantly, the graphene for the C-face is found to be *thinner* in the areas on top of the islands, consistent with a model in which sublimating Si atoms originate from the interface (and hence thicker graphene implies more material loss). For the Si-face a number of morphological features are found to interrupt the flat, uniform morphology of the graphene, including: surface pits, step bunches, and an apparent "secondary" graphitic surface phase. This secondary phase is observed as locally rough regions in the surface morphology. At low graphene formation temperature these regions can extend substantially over the entire surface, but at higher formation temperatures the regions shrink in size, until they produce only a faint finger-like pattern in the morphology as seen by AFM. We tentatively interpret the secondary phase as arising from excess carbon present *on top* of the surface (as opposed to at the graphene/SiC *interface*, where it would form well-ordered graphene).

4:00pm **GR+SS-MoA7 Nucleation of Epitaxial Graphene on SiC(0001), J.A. Robinson, D. Snyder, R. Cavalero, K. Trumbull, M. Wetherington, E. Frantz, M. LaBella, Z. Hughes, M.A. Fanton**, The Pennsylvania State University Electro-Optics Center

Currently, the most promising route for large area graphene, suitable for standard device fabrication techniques, is the sublimation of silicon from silicon carbide (SiC) at elevated temperatures (>1200 °C). Prior to graphene synthesis, SiC substrates are generally hydrogen etched at elevated temperatures to remove residual polishing damage. However, this process can result in significant step bunching, and lead to large terrace step heights. We utilize various surface preparation conditions, Raman spectroscopy, and atomic force microscopy to investigate the nucleation and growth of epitaxial graphene on SiC(0001). The location of graphene was identified using a WITec confocal Raman microscope (CRM) with a 488 nm laser wavelength, diffraction limited lateral resolution of ~ 340 nm, and spectral resolution of 0.24 cm^{-1} . The physical topography of the SiC substrate and graphene films were determined by atomic force microscopy using a Digital Instruments Nanoscope 3A.

We provide evidence that graphene not only nucleates at terrace step edges in the SiC surface, but also at surface defects such as residual surface damage from chemomechanical polishing, and screw dislocations. Prior to graphene synthesis samples were prepared in four manners: 1) *in situ*

hydrogen (H₂) etching; 2) *ex situ* potassium hydroxide (KOH) etching; 3) *ex situ* KOH and *in situ* H₂ etching; 4) No etch. Potassium hydroxide selectively etches defect sites on the SiC surface, leaving behind etch pits which serve as macro-defects in the SiC surface. Our monolayer epitaxial graphene was synthesized via Si-sublimation from the Si-face of semi-insulating SiC at 1325°C, 1x10⁻⁶ Torr. These conditions preclude the formation of graphene on SiC(0001) except at terrace step edges and other topological defects, effectively decorating the nucleation sites for subsequent characterization.

Samples with an *in situ* H₂ etch exhibit growth of graphene nearly exclusively at terrace step edges, while KOH etched samples exhibit graphene synthesis primarily at the etch pits and terrace step edges in the SiC surface. Those samples that experience no pre-treatment exhibit the highest surface coverage of any surface preparation, indicating that graphene grown on SiC(0001) nucleates at atomic scale defects on the SiC surface. This work provides evidence that defects in the form of dislocations, terrace step edges, and etch pits act as low energy nucleation sites for the growth of epitaxial graphene on SiC(0001). Finally, this work suggests that the growth of uniform graphene on SiC(0001) will be heavily influenced by the SiC substrate quality.

4:20pm **GR+SS-MoA8 The Effect of Adsorbates on the Electronic Properties of Graphene**, *E. Rotenberg*, Lawrence Berkeley National Laboratory **INVITED**

Epitaxially grown graphene films with various adsorbates have been prepared and investigated using angle-resolved photoemission spectroscopy (ARPES). Two regimes have been studied, which are differentiated by whether the adsorbates preserve the local symmetry of the graphene unit cell or not. For symmetry-preserving defects, such as adsorbed K or Ca atoms, the charge carriers in the graphene retain their metallic, Fermi liquid character, i.e. they can be described as single, weakly interacting “quasiparticles” with a relatively long lifetime as their energy approaches the Fermi level. (This is in contrast to strongly correlated systems where electron-electron scattering dominates the low energy dynamics) In such samples, ARPES measurements of the valence band can determine details of many-body interactions such as electron-phonon coupling. The second regime is followed by adsorbed atomic H atoms, which break the local lattice symmetry, and, for sufficiently high density, cause a dramatic breakdown in the quasiparticle picture, as evidenced by changes to the valence band spectrum. This, together with an accompanying metal-to-insulator transition, suggests that atomic H localizes the carriers, as described by Anderson’s theory.

*in collaboration with A. Bostwick, J. L. McChesney, T. Ohta, [LBNL], S. D. Kevan, [U. Oregon] K. V. Emtsev, Th. Seyller [U. Erlangen], and K. Horn [Fritz-Haber Institute]

5:00pm **GR+SS-MoA10 Low Temperature Halogen Assisted Synthesis of Epitaxial Graphene on SiC**, *M.A. Fanton, J.A. Robinson, B.E. Weiland, M. LaBella, K. Trumbull*, Penn State University

Graphene presents a host of remarkable physical and chemical properties that are uniquely beneficial for the development of nano-scale electronics and chemical sensors. However, high processing temperatures, and the resulting non-uniform surface topography significantly degrades the electronic properties of epitaxial graphene (EG). To minimize these issues a low temperature, atmospheric pressure, synthesis technique was developed that uses halogen species to extract Si from the SiC surface. This significantly minimizes surface roughening, and reduces substrate-induced strain in the graphene layer, which are major factors limiting material and device performance. The synthesis temperature of epitaxial graphene can be reduced to well below 1400°C by exposing the SiC substrate to halogenated (Cl, Br, F) gases. Our preliminary thermodynamic modeling shows that the formation of carbon on the surface of SiC can be accomplished using various halogen-hydrogen gas mixtures. The model shows that carbon formation on the SiC surface can be controlled using a combination of temperature, pressure, and halogen/hydrogen ratio. Using this technique, both the Si-face and C-face of 2” diameter SiC wafers have been graphitized at temperatures as low as 1150°C at a pressure of 600 Torr. Synthesis was accomplished in a SiC CVD reactor from Structured Materials. Temperatures ranged from 1150°C to 1350°C, making the process compatible with Si-based substrates. Growth pressures ranging from 0.1 to 600 Torr were explored, with higher pressures being preferred. The process atmosphere consisted of a mixture of hydrogen, argon, and halogenated gases such as HCl. The formation and structural quality of the epitaxial graphene was characterized using Raman spectroscopy, atomic force microscopy, transmission electron microscopy, and white light interferometry. Structural quality, as assessed by the Raman G’ and D+G peaks, was found to improve as the growth rate decreased and growth temperature increased. Growth rate at a fixed temperature and pressure was readily controlled via the halogen concentration and the halogen/hydrogen ratio as expected from the thermodynamic model. For thick carbon films the

growth rate on the C-face was typically 5 times higher than the growth rate on the Si-face. The impact of the halogen/hydrogen ratio was heavily dependent upon the source of the halogen species, which was also expected from thermodynamics. Transmission electron microscopy showed that the interface between the SiC and graphene was sharp and confirmed the number of layers present that was estimated by Raman spectroscopy. The surface roughness of graphene layers was on the order of 1-3nm.

5:20pm **GR+SS-MoA11 Galvanic Deposition of Au Nanoclusters on Epitaxial Graphene**, *M. Cerruti, N. Ferralis, R. Maboudian, C. Carraro*, UC Berkeley

Metallization of graphene surfaces are of crucial importance for the fabrication of metal-graphene contacts, and for surface functionalization via metallic nanostructures. In this paper, a novel method of selective deposition of Au clusters on graphene layers grown epitaxially on SiC substrate is presented. The size and the distribution of particles is regulated and fully controlled by the deposition process. From a combined use of scanning electron microscopy, x-ray electron spectroscopy and Raman microscopy, we propose that cluster nucleation takes place at the edges and defects in graphene domains, via oxidation of defects sites. The preferred nucleation indicates that a high level of selectivity is achieved by controlling the quality of the graphene film.

Surface Science

Room: M - Session SS1+EM-MoA

Semiconductor Surfaces and Interfaces I: Ge and III-V's

Moderator: M. Losurdo, IMIP-CNR, Italy

2:00pm **SS1+EM-MoA1 III-V MOS Device Performance Enhancement by Detection and Control of Individual Surface Oxidation States**, *C.L. Hinkle, M. Milojevic, A.M. Sonnet, E.M. Vogel, R.M. Wallace*, University of Texas at Dallas **INVITED**

Field effect transistors (FETs) remain at the heart of integrated circuit technology, and are forecasted to do so for at least the next decade. Silicon has been the material of choice for this purpose, but appears to be reaching significant performance limitations with further device dimension shrinking. As a result, the use of alternative semiconductor materials has again become of interest for FE T s. However, the native oxides (As-O and Ga-O) of these materials have been shown for more than thirty years to be of poor quality for metal-oxide-semiconductor (MOS) device performance. Furthermore, deposition of any gate oxide onto a clean III-V surface results in the oxidation of the substrate to detrimental effects. Despite the extensive research of III-V materials, there is still much to be understood about these oxides. In particular, the individual oxidation states of As (5+ and 3+) and Ga (3+ and 1+) are rarely considered despite evidence that they are quite different in forming defect states.

Recent work [1,2,3] will be presented on the detection and control of each of these surface oxidation states through carefully managed interfacial reactions and depositions on GaAs and InGaAs. The fabrication of MOS capacitors and FETs with these studied interfaces has led to a correlation between the spectroscopy and electrical measurements. An emphasis on controlling or eliminating each oxidation state through a variety of techniques has allowed for a detailed understanding of these native oxides and how each one affects device performance. The presence of the Ga 1+ oxidation state is spectroscopically detected for the first time at these interfaces and a dramatic increase in device performance is demonstrated by controlling the Ga 3+ surface concentration. This work is supported by the FCRP Materials, Structures, and Devices (MSD) Center, SEMATECH, FUSION funded by System IC 2010 (COSAR), The Texas Enterprise Fund, and NIST, Semiconductor Electronics Division.

[1] Hinkle et al., APL **94**, 162101 (2009).

[2] Sonnet et al., APL. **93** 122109 (2008).

[3] Hinkle et al., IEEE EDL **30**, 316 (2009).

2:40pm **SS1+EM-MoA3 Unpinning of In_{0.53}Ga_{0.47}As(001)-(4x2)/c(8x2) via Oxide Deposition for III-V MOSFETs**, *J.B. Clemens, S.R. Bishop, A.C. Kummel*, University of California, San Diego

The formation of a semi-ordered oxide passivation layer between hafnium oxide and In_{0.53}Ga_{0.47}As(001)-(4x2)/c(8x2) and InAs(001)-(4x2)/c(8x2) was studied using scanning tunneling microscopy/spectroscopy (STM/STS), and density functional theory (DFT) calculations. A passivation layer is needed to protect the surface from disruption during bulk amorphous oxide deposition for a high-κ gate insulator. Two methods of forming low coverage of HfO₂ were investigated: reactive oxidation of the e-beam deposited Hf metal and e-beam deposition from an HfO₂ target. STM results

show that Hf atoms must cluster to be reactive to O₂. DFT suggests there is a high tendency for Hf to displace substrate atoms, which is undesirable. Direct deposition of the oxide is a better method. At submonolayer coverage, STM has identified individual bonding sites for the HfO₂ molecule; the HfO₂ forms small structures of mostly monolayer height with a high nucleation density. Density functional theory (DFT) calculations have been employed to assign the bonding structure. The DFT simulations show that for HfO₂/InAs(001)-(4x2), the most likely sites are stable by about -4.5 eV and the calculated density of states (DOS) shows no evidence of Fermi level pinning (no mid-gap states). At submonolayer coverage, the HfO₂ molecule bonds via group III-oxygen bonds and group V-hafnium bonds. STS measurements of clean InGaAs(001)-(4x2) reveal that the surface has significant band bending, showing p-type character for both n-type and p-type samples. Deposition of > 1 ML of HfO₂ is enough to move the Fermi level towards the conduction band for n-type InGaAs(001)-(4x2), as shown in results of STS vs. HfO₂ coverage. For p-type material, the Fermi level remains near the valence band after deposition of HfO₂. These results are consistent with the Fermi level remaining unpinning. In addition, annealing effects are studied. At temperatures of 300 °C and above, ordered oxide structures are seen in STM which form rows in the [-110] direction. However, lower annealing temperatures of 200 °C and below are preferable for good STS results. Hafnium oxide, evaporated via electron beam deposition, likely creates some O₂ and HfO, which may react in an undesirable way with the semiconductor surface. For this reason, a method is also proposed to protect the surface during e-beam deposition via a CO₂ protecting layer at low temperature (90 K), which does not appear to perturb the surface.

3:00pm SS1+EM-MoA4 Formation and Structure of Alkaline Earth Template Layers for Oxide Epitaxy on Semiconductor (100) Surfaces. B. Lukanov, K. Garrity, J. Reiner, F.J. Walker, C.H. Ahn, S. Ismail-Beigi, E.I. Altman, Yale University

The finding that alkaline earth titanates can be epitaxially grown on Si and Ge(100) surfaces with atomically abrupt interfaces without oxidizing the semiconductor has spurred research into exploiting these materials for high k gate dielectrics, and for integrating new functionality into semiconductor devices. Attempts to epitaxially grow other oxides with similarly abrupt interfaces have thus far failed. It has been suggested that the initial interfacial layer formed by the reaction between the alkaline earths and Si and Ge is key to the success achieved with the alkaline earth titanates; therefore, we have been studying the interaction Sr and Ba with Ge and Si(100) with scanning tunneling microscopy (STM), complemented by density functional theory (DFT). At elevated temperatures, both Sr and Ba cause massive restructuring, indicative of surface alloy formation. Initial deposition causes an apparent etching away of the substrate dimers leading to dimer chains and islands on the surface. For Sr on Ge(100), increasing the coverage leads to an apparent c(4x4) structure decorated by bright spots that order only locally; the density of these bright spots decreases with increasing Sr coverage. The apparent c(4x4) structure ultimately gives way to a (3x2) structure that is characterized by periodic arrays of islands and trenches when it completely covers the surface. Electron diffraction data shows that continuing to raise the coverage causes a structural transformation to a (2x1) structure. On the atomic scale, STM images of the apparent c(4x4) and (3x2) structures vary dramatically with imaging bias; in particular changing the polarity of the bias voltage causes a contrast reversal where bright features in filled state images appear dim in empty state images and vice versa. Based on the observed bias dependence for Sr adatoms deposited at 300 K and simulated images derived from DFT calculations, a model of the (3x2) structure was developed in which Sr atoms replace every third row of Ge atoms on the surface. The striking periodic island and trench morphology is then associated stress relief of the (3x2) structure. The results clearly show that at elevated temperatures the template layer does not form through simple surface adsorption.

3:40pm SS1+EM-MoA6 STS and KPFM Investigation of InAs Pinning and Unpinning. W. Melitz, J. Shen, S. Lee, A.C. Kummel, University of California, San Diego

A combined scanning tunneling spectroscopy (STS) and Kelvin probe force microscopy (KPFM) study was performed on InAs(001)-(4x2) to elucidate the surface electronic properties since this surface is a leading candidate for III-V MOSFETs. KPFM provides higher energy resolution than STS, which is critical for studies of materials like InAs which have small band gaps (E_g=0.354 eV). Amplitude modulation (AM) mode KPFM provides especially high energy resolution (10 meV) and is free of tip induced band bending because of the low applied voltage (70 meV). STS spectra of InAs(001)-(4x2) consistently show pinning, with the surface Fermi level near the conduction band for both n-type and p-type samples even on nearly defect free surfaces. Using KPFM, the work functions for both n-type and p-type clean InAs(001)-(4x2) surfaces is 4.3 eV consistent with surface pinning. Using the electron counting rule, indium dimers in the trough are

sp² hybridized having a completely empty dangling bond. However the indium dimer atoms are positioned in a sp³ tetrahedral configuration; these strained bonding sites might be responsible for the pinning. If the pinning is solely due to the (4x2) reconstruction, it is expected that other reconstructions without indium dimers would be unpinning. KPFM was also performed on cross-sectional InAs, which is defect free and has no indium dimers. These results were consistent with the bulk values with a work function difference between n-type and p-type of 0.49 eV. By eliminate the buckled indium dimer states with a passivation layer the InAs(001)-(4x2) surface could become unpinning.

4:00pm SS1+EM-MoA7 Doping of InP Nanowires Studied by STM and X-ray PhotoEmission Electron Microscopy. M. Hjort, A.A. Zakharov, M.T. Borgström, E. Hilner, R. Timm, A. Fian, J.N. Andersen, E. Lundgren, L. Samuelson, A. Mikkelsen, Lund University, Sweden

Self-assembled III-V nanowire heterostructures could be key components in many future optoelectronic devices [1], for example solar cells [2]. To realize photovoltaics from these structures variable p- and n-type doping along the nanowires are a fundamental prerequisite. The active component in solar cells, the pn-junction, has been grown axially in InP nanowires with different p- and n-type doping levels. However determining specific doping levels, effects of the nanowire surfaces and junction abruptness and band alignment across the interface with any precision is very difficult. Recently we have shown that scanning tunneling spectroscopy on nanowires with high resolution is possible [3] and we are now combining this with synchrotron based photoemission methods.

We have examined InP nanowires with up to two axial pn-junctions with Spectroscopic PhotoEmission and Low Energy Electron Microscopy (SPELEEM), X-ray Photoelectron Spectroscopy (XPS) as well as Scanning Tunneling Microscopy/Spectroscopy (STM/S). These techniques have given us the possibility to probe not only the structure of the nanowires but also the electrical properties (such as doping level) with high lateral resolution.

With our different setups we can probe the local density of states, atomic scale structure and work function differences along the wires. We can clearly distinguish between the different n- and p-type parts of the nanowires with both the scanning probe as well as with the synchrotron radiation based techniques. Both surface and the inner regions of the wires can to some extent be probed by varying photon energies in SPELEEM or modifying the surface for STM. This gives us the opportunity to understand the device at many different levels and improve its future quality.

- [1]. L. Samuelson et al., *Physica E* **2004**, 21, 560-567
- [2]. M. T. Borgström et al., *Nanotechnology* **2008**, 19, 445602
- [3]. E. Hilner et al., *Nano Letters* **2008**, 8 (11), 3978-3982

4:20pm SS1+EM-MoA8 Direct Atomic Scale Imaging and Spectroscopy of the Interior and Exterior of III-V Nanowires. A. Mikkelsen, Lund University, Sweden **INVITED**

Free-standing III-V nanowires and nanotubes are likely to become central components in future electronics and photonics with applications in IT, life-science and energy[1]. A very wide variety of III-V materials and dopants can be self-assembled into complex axial and radial heterostructures - precisely tailoring their structure down to the atomic scale.

We have used Scanning Tunneling Microscopy /Spectroscopy (STM/STS) and X-ray PhotoEmission and Low Energy Electron Microscopy (XPEEM/LEEM) to study nanowires and nanowire surfaces. Previously we have developed the means to directly study the interior of III-V semiconductor nanowires by STM[2], and now we have also developed direct methods for studying also the exterior nanowire surfaces to the atomic scale with STM[3].

We describe several significant results on the fundamental limits to atomic scale interface precision in AlGaAs/GaAs nanowires heterostructures, STS measurements on the interior of these wires and new insights into the influence of the growth substrate. We present atomically resolved STM images of the outside surface of InAs nanowires with InP segments along with STS measurements on the clean surfaces. The imaged surfaces of InAs nanowires are quite intriguing as the wires grow in the wurtzite crystal phase, in contrast to the zincblende bulk phase. Further we present STM images and STS measurements of InP nanowire pn-junctions. Using XPEEM and XPS we have characterized III-V nanowire surface chemistry and electronic properties and investigated the influence of various ultra-thin dielectrics to reduce surface band-bending effects.

The structure and morphology of semiconductor nanowire surfaces down to the single atom level are significant in determining both growth and function of the wires. Diffusion and nucleation on the nanowire surfaces

will directly influence the final appearance of the wires, and it has been shown that transport and optical properties of semiconductor nanowires are to a considerable extent governed by their surfaces. Scanning Tunneling Microscopy is a great tool for imaging both geometric and electronic structure with high resolution, however direct atomically resolved STM studies of nanowire surfaces is very difficult. Still having overcome these problems (as in the present study) and by also applying synchrotron based spectroscopy/microscopy we obtain fascinating new insights into the interplay between nanowire growth, structure and function.

[1] C.M. Lieber and Z.L. Wang, MRS Bull. 32, (2007) 99

[2] A. Mikkelsen et al, Nature Mater. 3 (2004) 519 ; L. Ouattara et al, Nano Lett. 7 (2007) 2859

[3] E. Hilner, et al, Nano Lett., 8 (2008) 3978

5:00pm **SS1+EM-MoA10 Passivation of Ge(100) Surface Studied by Scanning Tunneling Microscopy and Spectroscopy**, *J.S. Lee, S.R. Bishop, A.C. Kummel*, University of California, San Diego

Finding a good passivant for Ge surface is critical for fabricating a Ge-based MOSFET device. Recent studies have shown that GeON or GeO₂ interfacial layers can partially passivate the Ge/high-k dielectric interface and improve the electrical properties of the device. Introducing N (GeO_xN_y or Ge₃N₄) suppresses the Ge outdiffusion from the passivation layer into the high-k oxide layer at elevated temperatures, thereby reducing the post annealing density of interface states between Ge and high-k gate oxide. To minimize the density of interface states, the GeO_xN_y or Ge₃N₄ must be formed with a minimal dangling bond density, which is challenging in a thermal oxidation or nitridation process. To investigate the bonding and electronic structures of Ge-N and Ge-O surface species, in-situ scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) experiments were performed after oxidation and nitridation. Direct nitridation was carried out on Ge(100) using an electron cyclotron resonance plasma source, both at room temperature and at 500°C. The nitridation at room temperature generated nitride sites, O sites (from trace water) and Ge adatoms which pin the surface Fermi level. The Ge adatoms are created because both O and N displace Ge surface atoms in order to bond at high coordination sites. These Ge adatoms can be removed by high temperature annealing. Nitridation at 500°C produced a highly ordered Ge-N structure on the surface without O sites or Ge adatoms, but the Fermi level of the n-type surface was still pinned near the valence band probably due to the surface defects caused by plasma damage. Oxidation of Ge(100) was studied using a differentially pumped H₂O dosing system and the results were compared with our previous study on O₂ dosing of Ge(100). The H₂O dosed surface showed dark -OH adsorption sites with very few Ge adatoms, while the O₂ dosed surface had the equal densities of Ge adatoms and O sites. Annealing the H₂O/Ge(100) surface to 300°C induces formation of bright Ge oxide sites which are slightly taller than Ge adatoms. However, both H₂O and O₂ dosing form GeO sites which are observed in STS to pin the Fermi Level. DFT calculations are being performed to determine the ordered nitride structure. In addition, the e-beam or ALD deposition of Ge₃N₄ or GeO₂ are being studied since they may form passivation layers without Ge displacement, plasma damage, and GeO, thereby unpinning the Fermi level.

5:20pm **SS1+EM-MoA11 Surface-driven Method for Incorporation of Mn into Ge Quantum Dots**, *C.A. Nolph, K.R. Simov, P. Reinke*, University of Virginia

Magnetically doped nanostructures and quantum dots are important building blocks in future spintronic devices. We study the feasibility of magnetic doping of Ge quantum dots with Mn, an element with a large magnetic moment. A surface-driven route for Mn incorporation in Ge quantum dots promises superb control of the doping process. The Ge quantum dots are known to grow by strain-driven self-assembly (Stranski-Krastanov growth). Two pathways for Mn-doping have been identified: firstly, trapping of Mn at the Si-Ge interface and incorporation during quantum dot growth, and secondly, the deposition of Mn on the Ge quantum dot surface and dissolution of Mn during an annealing process. The first route requires a precise control of the Mn-bonding state at the Si(100) 2x1 substrate prior to the growth of quantum dots. Mn was deposited on Si(100) 2x1 and the surface phase diagram was determined across several temperature regimes and monitored with scanning tunneling microscopy. Mn-wire structures which formed at room temperature degrade and agglomerate to form Mn-clusters (115 - 270°C ± 30°C), then Mn moves into subsurface sites (316°C ± 38°C), and the onset of Mn-silicide formation is observed at about 342 - 416°C. This sequence is driven by the kinetics of the surface reaction between Mn and Si. A photoelectron spectroscopy study of the Si-Mn and the Si-Mn-Ge interface yields further insight into the bonding at the respective interfaces. The second route to dope quantum dots, namely the room-temperature deposition of Mn on Ge quantum dots, reveals the formation of Mn clusters, whose position is

defined by the reconstruction of the Ge{105} facets. The diffusion of Mn on Ge(100) and Ge{105} facets, and into the Ge quantum dots is observed with STM during the annealing process. Our observations offer a comprehensive understanding of the Mn-interaction with all surfaces of relevance in the Si-Ge quantum dot system. The feasibility of the surface-driven route for Mn doping of Ge quantum dots will be discussed.

Surface Science

Room: N - Session SS2-MoA

Formation & Reactivity of Nanoclusters

Moderator: G.B. Fisher, University of Michigan

2:00pm **SS2-MoA1 Nanoplasmonic Sensing of Metal Hydride Formation and Catalytic Reactions on Metallic Nanoparticles**, *E.M. Larsson, C.M. Langhammer, B.H. Kasemo, I.L. Zoric*, Chalmers University, Sweden

A novel, nanoplasmonics-based optical sensing platform for real time studies of nanoparticle processes is described. Examples are presented for (i) surface catalytic reaction kinetics on nanoparticles and (ii) formation of a new phase in metal hydride forming nanoparticles. The remarkably sensitive and very versatile sensing platform consists of plasmonic sensing particles (Au nanodisks, D=76nm and h=40 nm, prepared on a transparent substrate), covered by a 10nm dielectric film onto which the nanoparticles to be studied are deposited (in the present case Pd or Pt, with a size range from 2 nm-10nm). The key to the sensing is utilization of localized surface plasmon resonances (LSPR). The LSPR of the sensing nanoparticle sensitively measures changes of the surface coverage (sensitivity <0.05ML) or the formation of the new phase in the studied nanoparticles via shifts in the LSPR extinction spectra. The versatility of this method is illustrated with the following examples:

- Hydrogen absorption/desorption (hydride formation) studies of Pd nanoparticles in the size range 2-10nm. The main result from these studies includes the size dependent thermodynamics (p-C-T diagram) and kinetics of the H/Pd nanoparticle (1-5 nm) system. The kinetics exhibit a power and power-exponential size dependence of the time scales for the hydrogen uptake and release processes. The uptake is in agreement with Monte Carlo simulations of diffusion controlled hydriding kinetics, while the release (desorption) is explained by the effect of surface tension on the activation energy for hydrogen desorption from the nanoparticle.
- Kinetic studies of CO and H₂ oxidation on Pt nanoparticles with particular emphasis on kinetic phase transition phenomena in these reactions. The latter occur as one varies reactant concentrations but keeps the total amount of reactants constant and are recognized by a sudden transition from oxygen covered nanoparticle surfaces at low CO (H₂) concentration, to high CO or H coverage for low O₂ concentrations,
- NO₂ storage and conversion to N₂ on Pt/BaO. In this case NO₂ storage and conversion kinetics is followed via changes in the LSPR resonance of the Au sensing particles, coated with a thin layer of BaO onto which Pt nanoparticles were deposited. Exposure of the sensor to the gas mixture of NO₂+O₂ leads to a conversion of BaO to Ba(NO₃)₂ (NO_x storage) leading to a change of refractive index of the material surrounding the sensing nanoparticle. This leads to a LSPR peak shift that is monitored. Exposure to H₂ converts the stored NO₂ to N₂. Reversible changes were monitored for such NO₂ oxidation/reduction cycles.

2:20pm **SS2-MoA2 On the Role of Pd Ensembles in Selective H₂O₂ Formation on PdAu Alloys**, *H. Ham, G. Hwang*, University of Texas at Austin

Bimetallic Pd-Au alloys have been found to significantly increase catalytic efficiency, compared to the monometallic Pd and Au counterparts, in various reactions including direct synthesis of H₂O₂ from H₂ and O₂ and production of vinyl acetate monomers. Recent evidence suggests that the reactivity of bimetallic catalysts would be governed by creation of unique mixed-metal surface sites [the so called ensemble effect] and/or electronic structure change by metal-metal interactions [ligand effect], while mechanisms underlying the alloying effect still remain unclear. Very recently, the role played by Pd monomers in the direct H₂O₂ synthesis has also been studied using density functional theory calculations, yet detailed reaction mechanisms associated with Pd atomic arrangements are still lacking. In this talk, we will present some recent theoretical results we have on the role of Pd ensembles in determining the selectivity of direct H₂O₂ synthesis. Using periodic density functional theory calculations, we find that the H₂O₂ formation selectivity can be governed by the spatial arrangements of Pd and Au surface atoms, particularly the availability of Pd monomers surrounded by less active Au atoms. Our calculations suggest

that the large activity difference between Pd and Au atoms is a key factor for selective H₂O₂ formation, by suppressing O-O bond scission. This work hints the importance of knowing how to properly tailor Au reactivity for achieving wanted reactions, while the relative activities of Au and Pd surface atoms can be a function of subsurface layer composition as well as catalyst size and shape.

2:40pm **SS2-MoA3 Well-defined, Highly Uniform Metallic Nano-Structures as Selective Heterogeneous Catalysts and Platforms for Chemical Characterization**, *S. Linic, Christopher*, University of Michigan
INVITED

I will present our recent work where we explored potential utilization of highly uniform metallic nano-structured materials as selective heterogeneous catalysts. The advantage of these materials compared to conventional catalytic materials is that their structure can be controlled with almost atomic precision, and that it is possible to synthesize highly homogeneous structures. We demonstrated some of these advantages recently when we showed that well-defined, tailored Ag nano-structures are much more selective in heterogeneous epoxidation of ethylene to form ethylene oxide (EO) (ethylene + ½ O₂ → EO) than conventional industrial catalysts.

We showed using quantum chemical Density Functional Theory (DFT) calculations, where we studied critical elementary chemical steps that govern the selectivity to EO in the process, that the Ag(100) surface should be inherently more selective than the Ag(111) surface. We note that catalytic particles, synthesized using conventional synthesis procedure and currently used in commercial ethylene epoxidation process, are dominated by the (111) surface. To synthesize Ag nano-structures which are dominated with the Ag(100) faces, we employed a synthesis procedure which uses organic stabilizer molecules to direct the growth of the nano-structure in a particular direction and to control the surface facets that terminate the nano-structure. This synthetic strategy allowed us to synthesize well-defined and highly uniform Ag nano-wires and nano-cubes which are dominated by the (100) facet. Subsequent experiments showed that Ag nano-wires and nano-cube catalysts can achieve selectivity to EO, which is, at differential conversion, by ~ 40 % higher than for conventional Ag catalysts.

We have also recently started exploring these metallic nano-structures as possible platforms for chemical characterization. The features of these nano-structures that are particularly appealing are: (i) the nanostructures are well defined on atomic level, and their surface to volume ratio is fairly high, which makes these structures inherently better suited for the studies of surface chemical processes compared to traditional single crystal model systems, which are while very well defined, characterized by low surface to volume ratio, (ii) we can synthesize the nanostructures with high degree of uniformity in size and shape, which rules out possible effects due to diversity in size and shape, i.e. these, (iii) the nanostructures are effective scatterers of electromagnetic radiation which make them suitable as platforms for a number of chemical characterization techniques including surface enhanced Raman (SERS) or IR spectroscopies. We will demonstrate the utility of the nano-structures for chemical characterization by a way of an example, where we monitored in-situ ethylene epoxidation.

3:40pm **SS2-MoA6 2009 AVS Peter Mark Memorial Award Lecture - Towards the Understanding of Catalytic and Vibrational Properties of Metal Nanostructures**, *B.R. Cuenya**, University of Central Florida
INVITED

Metallic nanostructures are of great interest in many scientific fields due to their novel size-dependent physical and chemical properties. The origin of the enhanced catalytic reactivity and selectivity displayed by small metal nanoparticles is yet to be explained. However, it is generally agreed that the design of the next generation of nanocatalysts requires detailed knowledge of the correlation between their reactivity and their physical properties such as morphology, electronic structure, chemical composition, and interactions with their support. Intriguing effects including phonon confinement and phonon localization at interfaces have also been observed in low dimensional systems. Such modifications of the vibrational density of states of nanoscale materials are of scientific and technological relevance, because they profoundly affect their thermodynamic properties. In addition, their understanding could help further our insight in the field of catalysis, since phonons might play a decisive role in certain chemical processes. To systematically study these effects, homogeneous and size-selected nanostructures are needed. Diblock-copolymers can aid the synthesis of such well-defined nanoscale systems.

The first part of my talk will illustrate the formation, stability, as well as the electronic and catalytic properties of size- and shape-selected Au, AuFe, Pt, and Pt-M (M = Au, Fe, Ru and Pd) nanoparticles synthesized by micelle

encapsulation. CO oxidation and alcohol decomposition and oxidation have been used as model reactions. Emphasis will be given to the role of the nanoparticle support and the oxidation state of the active catalytic species in their reactivity.

In addition to changes in reactivity, nanostructuring materials also affects their vibrational properties. The second part of my talk will discuss the size- and composition-dependent vibrational dynamics of ⁵⁷Fe, ⁵⁷FePt, and ⁵⁷FeAu clusters as well as of nanostructured metal multilayers prepared by molecular beam epitaxy in UHV. The phonon density of states of these systems will be extracted from nuclear resonant inelastic X-ray scattering measurements. An enhancement of the density of low- and high-energy phonon modes as well as non-Debye-like behavior was observed on ⁵⁷Fe clusters. The latter effects were found to depend on the chemical nature of the surface shell on the nanoclusters. Thickness-dependent phonon confinement and interface localization effects were detected on nanoscale ⁵⁷Fe/M multilayers (M = Cu, Pd or Ag). All these effects show the unique physical properties of metal nanoparticles, and their promise in technological applications.

Website: <http://www.physics.ucf.edu/~roldan>

4:20pm **SS2-MoA8 Growth, Composition and Surface Chemistry of Ni-Au Clusters on TiO₂(110)**, *D.A. Chen, S.A. Tenney, J.S. Ratliff, C.C. Roberts*, University of South Carolina

Scanning tunneling microscopy (STM) studies show that bimetallic Ni-Au clusters supported on TiO₂(110) are formed by deposition Au on top of Ni clusters. Due to the higher mobility of Au compared to Ni atoms on TiO₂(110), deposited Au is nucleated at existing Ni clusters. Low energy ion scattering experiments demonstrate that the surface of the bimetallic clusters is predominantly Au for compositions above 50% Au, but 10-15% Ni also exists at the surface. The presence of Ni at the surface is in contrast to the expected Ni core-Au shell structure based on bulk thermodynamics; the large bulk miscibility gap for the two metals and the lower surface free energy of Au compared to Ni predicts that only Au should be at the cluster surface. Furthermore, adsorption of CO onto the Ni-Au clusters appears to induce the diffusion of Ni to the cluster surface. After annealing the Ni-Au clusters to 800 K and above, the clusters become encapsulated by stoichiometric titania. Although Ni and Au clusters annealed to 1000 K are roughly the same size, the addition of Ni to the Au clusters suppresses cluster sintering.

4:40pm **SS2-MoA9 Deposition of RuSn Nanoparticles onto a Al₂O₃/Ni₃Al(111) Surface from a Gas Phase Organometallic Precursor**, *A. Uhl, University of Illinois at Chicago, E. Trufan, R.D. Adams, University of South Carolina, R.J. Meyer, M. Trenary*, University of Illinois at Chicago

Scanning tunneling microscopy (STM) was used to characterize RuSn nanoparticles deposited from a gas phase organometallic precursor (Ru₃(CO)₉(μ-SnPh₂)₃) onto an Al₂O₃ film grown on a Ni₃Al(111) substrate. This novel method allows for the specific preparation of small metal clusters that range between single atoms and larger, bulk-like particles. It also assists in bridging the gap between previous studies based on metal evaporation and industrial catalysis, where the use of precursor compounds for the active species is common. The STM images of the Al₂O₃/Ni₃Al(111) substrate prior to the exposure of the precursor show two distinct areas, with the first one exhibiting the dot structure of the alumina film, as reported in the literature. The second area does not exhibit any regular structure. After exposing the sample to the precursor at room temperature, the precursor was found to adsorb preferentially onto the second area, but also on the first area in significant amounts. In a subsequent series of images acquired for increasingly higher annealing temperatures, the discrepancy between the two areas in the interaction with the adsorbates is strongly increased. While the surface with the dot structure becomes almost fully depleted of the adsorbates, except for a few small (up to 3 nm in diameter) and roundish protrusions, the other area is covered by larger polygonal protrusions. Similarly shaped depressions in the surface are observed along with the protrusions. A control experiment in which the bare Ni₃Al(111) surface was exposed to the precursor indicates that the second area of the Al₂O₃/Ni₃Al(111) surface consists of patches of bare metal. A striking difference between the protrusions on the oxide and the metal is that the size of the latter increases dramatically with increasing annealing temperature, while the former do not grow at all. Nevertheless, both features are observed even up to 925 K, from which it is concluded that the annealing removes the ligands from the metal centers of the precursor molecules, after which the metal nanoparticles can form. These results show that by using an organometallic precursor, small uniform metal nanoparticles with high thermal stability can be successfully deposited onto an oxide thin film. This paves the way for subsequent studies of the surface chemistry associated with model oxide-supported metal catalysts consisting of metal nanoparticles of a uniform size.

* Peter Mark Memorial Award Winner

5:00pm **SS2-MoA10 Formation, Thermal Stability and In-situ Gas Phase Catalytic Properties of Supported Au, Fe, and Au_xFe_{1-x} Nanoparticles**, L.K. Ono, A. Naitabdi, B. Roldan Cuenya, University of Central Florida

Metal-loaded diblock-copolymer micelles have been used to synthesize size-selected self-assembled Au, Fe, and Au-Fe nanoparticles (NPs). In-situ scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the formation and thermal stability of Au_xFe_{1-x} (x = 1, 0.8, 0.5, 0.2, 0) NPs supported on TiO₂(110) [1]. Upon step-wise annealing from 300°C to 1060°C, a remarkable thermal stability of the Au-Fe NPs was observed, maintaining their original hexagonal spatial arrangement on the TiO₂ surface up to 900°C. A majority phase of a gold-iron alloy (solid solution) was achieved for our Au_{0.5}Fe_{0.5} NPs in the temperature range of 700°C - 800°C, and for Au_{0.2}Fe_{0.8} NPs at 800°C, while a phase mixture of bcc Fe and Au-Fe alloy was observed for the Au_{0.8}Fe_{0.2} system at 800°C - 900°C. For all samples the segregation of Au atoms towards the NP surface was detected upon high temperature annealing (800°C) in vacuum. Nearly complete Au desorption was observed by XPS at 900°C for Au_{0.2}Fe_{0.8} NPs, at 1000°C for Au_{0.5}Fe_{0.5} NPs, and at 1060°C for Au_{0.8}Fe_{0.2} NPs. The enhanced thermal stability of Au in the Au_{0.8}Fe_{0.2} NPs is believed to be related to the formation of core(Fe)/shell(Au) structures. Furthermore, contrary to the case of pure Fe or Fe-rich NPs where nearly complete Fe desorption or Fe diffusion into TiO₂ was observed at 1000°C, an Fe signal was detected at this temperature for the Au-rich samples (Au_{0.8}Fe_{0.2} and Au_{0.5}Fe_{0.5}).

The reactivity of our pure Au, pure Fe, bimetallic Au-Fe and a sample with a mixture of pure Au and pure Fe NPs will be compared via in-situ (UHV) temperature programmed desorption measurements. CO oxidation has been used as probe reaction.

[1] A. Naitabdi, L.K. Ono, F. Behafarid, B. Roldan Cuenya, J. Phys. Chem. C 113 (2009) 1433.

5:20pm **SS2-MoA11 Secretive Lives of Multi-component Nanoparticles during Reactions**, F. Tao*, M. Grass, D. Butcher, J.R. Renzas, Y. Zhang, C. Tsung, S. Aloni, M. Salmeron, G.A. Somorjai, Lawrence Berkeley National Lab

The bimetallic catalyst is one important category of heterogeneous catalysts for numerous industrial processes and energy conversion. Surface structure and chemistry of three bimetallic catalysts, Rh-Pd, Rh-Pt, and Pd-Pt nanoparticles during catalysis, oxidation, and reducing reactions have been systematically studied in-situ using XPS in a Torr pressure range and high resolution TEM. The Rh_xPd_{1-x} and Rh_xPt_{1-x} nanoparticles undergo reversible changes in both atomic fractions and chemical states corresponding to the switch of reaction environments between oxidizing and reducing conditions. Rh atoms in Rh_xPd_{1-x} and Rh_xPt_{1-x} segregate to surface layers and are largely oxidized in oxidizing conditions while in reducing atmospheres the Pd atoms in Rh_xPd_{1-x} and Pt atoms in Rh_xPt_{1-x} diffuse to the surface regions and Rh atoms are largely reduced. In contrast to Rh_xPd_{1-x} and Rh_xPt_{1-x}, no significant segregation of Pd or Pt atoms was found in Pt_xPd_{1-x} nanoparticles; Pd atoms are alternatively oxidized and reduced under oxidizing and reducing conditions, whereas Pt atoms do not. The capability of restructuring nanoparticles through chemical reactions illustrates the flexibility of the structure of bimetallic nanoparticle catalysts and suggests a new method for the development of new catalysts.

Reference: F. Tao et al. 322, 932 (2008)

Tuesday Morning, November 10, 2009

Surface Science

Room: M - Session SS1-TuM

Oxide Surfaces: Reactions and Structure

Moderator: R.L. Kurtz, Louisiana State University

8:00am **SS1-TuM1 UV Induced Work Function Change of Oxide Surfaces**, *S. Gutmann, M. Wolak, M. Conrad, M.M. Beerbom, R. Schlaf*, University of South Florida

The work function of conductive oxide thin films is an important parameter determining the band line-up at interfaces to active electronic materials in optoelectronic devices. The presented experiments aimed at the measurement of the work function of indium tin oxide (ITO), and nanocrystalline TiO₂ and ZnO thin films using photoemission spectroscopy. Traditionally, ultraviolet photoemission (UPS) is used to measure the work function of solid surfaces by means of the photoelectric effect. Such measurements are able to yield absolute work function values.

Our experiments showed that UPS measurements reduce the work function of oxide surfaces by up to 0.5 eV. This effect occurs within seconds, effectively preventing measurements of the 'true' work function of surfaces prior to UV exposure. A similar effect is observed when exposing oxide surfaces to x-ray doses typical for x-ray photoemission spectroscopy measurements. It was possible to quantify these effects through the use of low intensity XPS (LIXPS) based work function measurements, which allow a time-window sufficiently long for work function measurements without significantly influencing the work function. The experiments suggest that the work function reduction occurs through the hydroxylation of oxygen vacancies in the oxide surfaces by means of photochemical dissociation of adsorbed water molecules.

8:40am **SS1-TuM3 Low-energy Alkali Ion Scattering Studies of Bi₂Sr₂CaCu₂O_{8+δ}**, *R.D. Gann*, University of California, Riverside, *J. Wen, Z. Xu, G.D. Gu*, Brookhaven National Laboratory, *R.Q. Wu*, University of California, Irvine, *J.A. Yarnoff*, University of California, Riverside

The high-*T_c* cuprate BSCCO-2212 is investigated with low energy (0.5-10 keV) alkali ion scattering, which is an extremely surface-sensitive technique that can reveal compositional, structural and electronic information about a surface. Samples were cleaved at liquid nitrogen temperature in ultra-high vacuum, and time-of-flight spectroscopy was used to measure charge-resolved energy spectra of the scattered ions. Clean surfaces were shown to be terminated by BiO, and the inhomogeneous surface potential of the as-cleaved surface was revealed by the angular dependence of the neutralization. The effect on local potential due to adsorption of alkali and halogen species was ascertained by neutralization measurements and verified with density-functional theory. Deliberate damage induced by 500 eV argon sputtering revealed a gradual disordering of the surface as underlying metallic species diffuse upward, rather than layer-by-layer etching, as earlier SIMS studies have suggested. A detailed view of the surface termination opens the door for studies of other, similarly layered materials such as Bi₂Se₃.

9:00am **SS1-TuM4 Termination and Identification of Surface Species on the Magnetite (111) Surface Studied by Scanning Tunneling Microscopy**, *T.K. Shimizu, Y. Kim*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Besides its magnetic properties, magnetite exhibits an interesting first order phase transition called the Verwey transition (*T_V*~120 K). Although there have been many atomistic investigation using scanning tunneling microscopy (STM) at room temperature (RT), the most stable structure of Fe₃O₄(111) has not been yet in complete agreement. By employing STM and scanning tunneling spectroscopy (STS) at 77 K, we have studied the Fe₃O₄(111) surface using a naturally grown single crystal. STM images show a hexagonal lattice with an approximately 0.6 nm periodicity, no remarkable difference from RT observations. Based on the comparison of STS with a theoretical calculations, this surface can be assigned to the Fe_{et} termination, where the layer of Fe cations at the tetrahedral site terminates the crystal, supporting results of several early studies. In addition to these findings, we found two distinct features on the as-prepared surface. These features are considered to be the same species as those seen in the RT STM study [1] from the site and the bias dependence of their appearances. We were able to obtain direct evidence of their origin being water by intentionally adsorbing water both at 77 K and at RT, in agreement with previous predictions [1]. For instance, by injecting tunneling electrons into as-dosed intact water molecules at 77 K, we could induce reactions to one

of the originally observed species. In contrast to RT experiment, however, their diffusion requires much higher energy, which may be explained by the inefficient electron-phonon (e.g., OH stretching mode) coupling due to the smaller number of electronic states available near the Fermi level below the Verwey transition temperature.

[1] Sh. Shaikhutdinov and W. Weiss, *J. Mol. Catal. A: Chem.* 158, 129-133 (2000)

9:20am **SS1-TuM5 Scanning Tunneling Microscopy Investigation of the Vanadium Dioxide Surface and Its Related Metal-Insulator Transition (MIT)**, *W. Yin, P. Reinke, S. Wolf*, University of Virginia, *C. Ko, S. Ramanathan*, Harvard University

Vanadium dioxide (VO₂) is one of the most interesting thermochromic materials exhibiting a metal-insulator transition (MIT) close to room temperature (*T_{MI}* ≈ 340 K). This study presents an observation of the progression of the MIT with scanning tunneling microscopy and spectroscopy as a function of temperature with high spatial resolution. The high-quality VO₂ thin films used in this study were deposited on (0001) Al₂O₃ substrates using a sputtering technique. Electron tunneling current (conductivity) maps showed that the material surface was semiconducting before heating, and highly metallic above *T_{MI}*. The spatial distribution of bandgaps, semiconducting and metallic regions, is compared to the sample topography, and a model describing the progression of the MIT across the surface will be presented. In particular, the role of the chemical modification and reduction of the surface during heating will be discussed, and compared to the stability of the bulk phase. The surface was still partially metallic after cooling down but tended to recover its semiconducting nature over a long period of time. We attribute such irreversible surface electrical changes to the loss of oxygen and the strain relaxation in the VO₂ lattice. The spatial distribution of bandgaps indicates that the phase transition probably started from grain boundaries and the VO₂ surface exhibited an inhomogeneous behavior both above *T_{MI}* and after heat treatment.

9:40am **SS1-TuM6 The Adsorption and Reaction of Alcohols on Poorly Crystalline γ-Al₂O₃ Surfaces**, *J. Kwak, J. Szanyi, C. Peden*, Pacific Northwest National Laboratory

γ-alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for other catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-alumina, and its formation and thermal stability have been and continue to be the subject of a considerable amount of research, including attempts to prepare model surfaces via the controlled oxidation of NiAl alloy single crystals. However, due to the low crystallinity and very fine particle size of γ-alumina, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ-alumina, relating its surface structure to the origin of Lewis and Brønsted acidity has been of considerable interest and has been studied by solid state NMR and FTIR spectroscopies, and most recently by theoretical calculations. In this presentation, we describe recent studies using ultra-high resolution NMR spectroscopy as an especially useful probe of the γ-alumina surface structure, and its relevance to catalytic behavior. In particular, we correlate the NMR spectra with measurements of the adsorption and reaction of alcohols. In this way, we demonstrate a strong dependence of this chemistry on the presence of specific 5-coordinate Al³⁺ ions. These sites, in turn are a function of the dehydration temperature of the alumina material before use. From these correlations, we are able to explain a considerable number of prior observed phenomena.

10:40am **SS1-TuM9 The Growth and Structure of Ceria Islands on Cu(111)**, *F. Yang, J. Graciani, S. Senanayake, J.B. Park, D.J. Stacchiola, P.J. Liu, J. Hrbek, J.A. Rodriguez*, Brookhaven National Laboratory

Ceria-based catalysts are widely used for a number of catalytic reactions, such as the water gas shift reaction (CO + H₂O → H₂ + CO₂) or CO oxidation (CO + 1/2 O₂ → CO₂). Recently, it has been reported that ceria nanoparticles supported on Au(111) are much more efficient for the water gas shift reaction than the oxide or metal alone. In this work, we investigate the CeO_x/Cu(111) system as a model for Cu-CeO₂ water-gas shift catalysts. Using scanning tunneling microscopy (STM), we study the nucleation and growth of ceria islands on the Cu(111) surface. Ce is vapor-deposited on Cu(111) under an atmosphere of O₂ (~ 1 × 10⁻⁷ Torr) at different temperatures (300-600 K). We show how the geometric structures of ceria islands could be changed by altering the growth kinetics. We also show the evolution of the morphology when the CeO_x/Cu(111) surface interacts with CO or H₂O. Through an interplay with density functional theory (DFT) and

X-ray photoelectron spectroscopy (XPS), the structure of supported ceria islands will be described.

11:00am **SS1-TuM10 Morphology and Electronic Structure of Ultrathin Oxide Films on Pt₃Ti(111)**, *M. Moors, S. Le Moal, C. Becker, K. Wandelt*, University of Bonn, Germany

TiO₂ supported metal catalysts are known to have interesting catalytic properties, e.g. for oxygen reduction of water in fuel cells and for CO hydrogenation. The formation of titanium oxides on Pt-Ti alloy surfaces is one promising approach to develop new TiO₂ based model catalysts. In this work the crystallographic and electronic structure as well as the surface composition of ultrathin titanium oxide films grown on a Pt₃Ti(111) single crystal surface have been investigated as a function of oxidation temperature (700 K to 1000 K) and oxygen exposure (up to 9000 L) using Low Energy Electron Diffraction (LEED), Ultraviolet Photoelectron Spectroscopy (UPS) and Auger Electron Spectroscopy (AES). The composition of the titanium oxide films formed on this alloy surface strongly depends on the preparation conditions. From AES and LEED measurements two different stable oxide phases have been identified at high temperatures (above 900 K), depending on the oxygen exposure. At lower oxygen exposures (below 135 L) the most stable structure is a quasi-hexagonal one ($a = 3.35 \text{ \AA}$, $b = 3.25 \text{ \AA}$, $\alpha = 124^\circ$) rotated by 4° with respect to one of the substrate symmetry axes. The $p(2 \times 2)$ pattern, which is attributed to the Pt₃Ti(111) substrate, is still visible after this mild oxidation; suggesting that some areas of the substrate remain unoxidized. At higher oxygen exposures (between 220 L and 9000 L) the predominant structure is a commensurate hexagonal structure ($a = 3.20 \text{ \AA}$) rotated by 4° with respect to one of the substrate symmetry axes. In this case the $p(2 \times 2)$ substrate structure is no longer visible. Apart from these two stable structures, several additional LEED patterns have been observed, which are related to metastable oxide structures. However, this great diversity of LEED patterns is not reflected in the UPS measurements. Comparing the clean Pt₃Ti(111) surface with Pt(111) shows a significant broadening of the Pt related intensity between 1 and 4 eV as well as the appearance of a strong Ti related signal around 6 eV. For the clean Pt₃Ti(111) surface a work function of 5.02 eV has been determined. Oxidizing the alloy leads to additional peaks at a binding energy of 5.5 and 7.5 eV. The work function of the oxidized surface is increased by 0.3 eV related to clean Pt₃Ti(111). Remarkably, neither the spectral shape nor the work function significantly depends on the temperature and oxygen pressure used during oxidation.

11:20am **SS1-TuM11 Facile C-H Bond Cleavage of Propane on a PdO(101) Thin Film**, *J.F. Weaver, C. Hakanoglu, S.P. Devarajan, A. Minter*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of alkanes under oxygen-rich conditions, but difficulties in preparing well-defined surfaces have hindered fundamental studies of PdO surface chemistry. We have recently found that a high-quality PdO(101) thin film can be grown on Pd(111) in ultrahigh vacuum by oxidizing the metal at moderate temperature using an oxygen atom beam. In this talk, I will discuss recent results showing that propane adsorbs into a strongly-bound molecular state on PdO(101) and undergoes facile C-H bond cleavage below 200 K. The adsorbed hydrocarbon fragments are completely oxidized by the PdO surface above about 400 K, yielding gaseous CO₂ and H₂O during temperature-programmed experiments. From measurements of product yields as a function of the surface temperature, we show that the initial C-H bond cleavage of propane on PdO(101) occurs by a precursor-mediated mechanism with a negative, apparent activation energy, and present evidence that the strongly bound molecular state serves as the precursor to the initial dissociation. We suggest that a donor-acceptor interaction between a C-H bond(s) of the propane molecule and a coordinatively unsaturated Pd atom enhances the binding of propane on PdO(101), beyond that expected for physisorbed molecules, and facilitates C-H bond activation. Finally, I will summarize recent experimental and computational results which show that CH₄ and H₂ molecules also interact strongly with PdO(101) through dative bonding. The activation of propane on PdO(101) is analogous to alkane reactions with mononuclear transition metal compounds for which alkane sigma complexes act as key intermediates.

11:40am **SS1-TuM12 Investigation of Oxygen Embedment and Surface Restructuring on the Cu(100) Surface by Density Functional Theory Calculations**, *M. Lee, A. McGaughy*, Carnegie Mellon University, *J. Ren, J.C. Yang*, University of Pittsburgh

When the oxidation of a Cu(100) surface reaches 0.5 monolayer (ML) oxygen coverage, the surface structure transforms into the missing-row reconstruction. With further oxygen exposure, cuprite (Cu₂O) islands nucleate and then grow both into and along the surface. To investigate the early stages of Cu(100) oxidation, we apply density functional theory calculations to study the oxygen embedment into the surface using the nudged elastic band (NEB) method. We find that as the surface oxygen

coverage increases on the unreconstructed Cu(100) surface, the energy barrier for embedment decreases and the oxygen embedment is energetically favorable at coverages of 0.75 ML and 1.0 ML. At 0.5 ML coverage, the embedment energetics vary with surface morphology [$c(2 \times 2)$, missing-row reconstruction, and $c(2 \times 2)$ with 0.25 ML disordered vacancy structures], but in all cases the embedment is not energetically favorable. At 0.625 ML coverage, however, the oxygen embedment is favorable and we investigate the energetics for embedment into the missing row reconstruction through the missing row and alternate paths. We find that oxygen embedment through the missing row is more probable. We predict that oxygen sub-surface diffusion will occur because the energy barrier is comparable to that for surface diffusion. To study the intermediate states between the missing-row reconstruction and cuprite island nucleation, we are investigating various combinations of on- and sub-surface oxygen adsorbed structures by DFT calculation. We find that an additional oxygen molecule plays a role in the surface restructuring not only morphologically but also energetically for the unreconstructed Cu(100) surface. We are using a similar methodology to investigate the role of the additional oxygen molecule for surface restructuring on the missing-row reconstructed surface.

Surface Science

Room: N - Session SS2-TuM

Reactions on Metals and Bimetallics

Moderator: S. Chiang, University of California, Davis

8:00am **SS2-TuM1 Surface Structure of the Pd-H System**, *K.F. McCarty*, Sandia National Laboratories, *B. Santos*, Universidad Autónoma de Madrid, Spain, *T. Herranz*, Instituto de Química-Física "Rocasolano", Spain, *J.I. Cerda, J.M. Puerta*, Instituto de Ciencias de Materiales de Madrid, Spain, *J. de la Figuera*, Instituto de Química-Física "Rocasolano", Spain

Palladium hydride, PdH, is the model transition-metal hydride. Surface-science studies of PdH are scarce for two reasons. First, hydrogen pressures in the 10⁻⁵ of torr range are needed to form PdH near room temperature. Second, the expansion of the lattice that occurs during hydride formation tends to destroy Pd single crystal. To overcome this latter problem, we use thin epitaxial films of Pd(111) on Ru(0001) and W(110) to examine the surface science of the Pd-H system. To achieve an effective higher hydrogen pressure, we expose the Pd films to atomic H. We use low-energy electron diffraction (LEED) to characterize the Pd surface after H exposure. By performing the LEED in a low-energy electron microscope (LEEM), we are able to collect diffraction data from the same, atomically flat regions before and after H exposure. Detailed analysis of the LEED IV curves shows that exposure to atomic H at about 200K expands the interlayer spacing of the top two Pd layers but does not affect deeper layers. We interpret these changes as the formation of a surface hydride. Exposure to atomic H while cooling from above room temperature also produces the surface hydride. The lack of diffusion deeper into the film suggests that an energy barrier inhibits diffusion past the second Pd layer. The synthesis of a bulk hydride was attempted by exposing a Pd film to 40 torr of hydrogen and then reducing the pressure after cooling. The resulting material presented sharp, 3-fold diffraction patterns with an IV response different than the surface hydride. We will discuss the structure of this material, which we tentatively assign to a bulk PdH.

8:20am **SS2-TuM2 Surface-catalyzed O₂ Adsorption on Quantum Thin Films**, *J. Kim, A. Khajetoorians*, The University of Texas, Austin, *W.G. Zhu, Z.Y. Zhang*, Oak Ridge National Laboratory, *C.K. Shih*, The University of Texas, Austin

Pure crystalline Pb is well known to be inert with respect to oxygen gas. By using scanning tunneling microscopy we demonstrate that the oxygen adsorption on Pb films is greatly increased by Cs adsorbates acting as catalysts. Our previous studies show that Cs atoms can be easily incorporated into the surface layer of thin Pb films through a substitutional process when they are evaporated at low temperature (100 – 120 K). In addition, this Cs-Pb surface alloying process works cooperatively with the quantum size effect, leading to formation of nano-islands. This study explores the effect of the surface alloying on the oxidation. With only a minute concentration of Cs (0.004 ML coverage), we found a great enhancement of surface oxidation rates. Theoretical DFT calculations have revealed that the oxygen adsorption energy is greatly enhanced at the Cs substitutional sites. Subsequent oxygen exposures lead to great enhancement of oxidation which can be identified as PbO. Furthermore, we have explored the effect of temperature on the formation of Cs-Pb alloy and its consequences for the oxidation of Pb.

8:40am **SS2-TuM3 Surface Reactions on Model Gold Catalysts**, *C.B. Mullins*, University of Texas at Austin **INVITED**

We have studied model gold catalysts consisting of gold clusters supported on planar titania supports and Au single crystalline samples employing standard UHV surface chemical probes in addition to molecular beam techniques. In this talk I will focus on our results relating to enhanced CO oxidation by adsorbed water and the oxidation of alcohols employing single crystalline bulk gold. Briefly, we have found that adsorbed water can greatly enhance CO oxidation on oxygen pre-covered bulk gold at low temperatures. Additionally, we have found that atomic oxygen pre-covered Au(111) can partially oxidize ethanol, 1- and 2-propanol, and 2-butanol to their respective ketone or aldehyde with high efficiency and selectivity.

9:20am **SS2-TuM5 Oxidative Removal of Carbodiimide (NCN) and Isocyanate (NCO) Species from Cu(001) Surfaces**, *E.Z. Ciftlikli, J. Lallo, E.Y.-M. Lee, S. Rangan, L. Tskipuri, R.A. Bartynski, B.J. Hinch*, Rutgers University

Adsorbed isocyanate (NCO) species on Cu(001) undergoes oxidation, in the presence of O_(a), at temperatures as low as 373K. N_(a) remains and CO_{2(g)} evolves. On the other hand, a NCO/Cu(001) surface, in the absence of any other coadsorbates, is stable up to ~523K. Above this temperature, a bimolecular decarboxylation reaction is induced, which produces CO_{2(g)} and a surface bound carbodiimide (NCN) species alone. RAIRS measurements confirm a surface parallel species with an "sp" hybridized carbon atom. The introduction of oxygen at room temperature on NCN/Cu(001) leads to the reappearance of NCO species on the surface. The apparent yield of reformed NCO is not simply in proportion to the initial NCO dose levels. The chemistry of the NCO species is affected by the likely coadsorbates; N_(a), O_(a), and NCN_(a). The ν₂(NCO) bands observed in RAIR spectra of these partially oxidized surfaces, apart from being complex in shape, display a significant blue shift with respect the ν₂(NCO) modes observed when similar quantities of NCO are adsorbed on coadsorbate-free surfaces. In addition, the annealing of these surfaces to 473K indicates only a partial further oxidation of NCO. Even at excessive O₂ doses, NCO is not fully oxidized by 473K. A further annealing to ~ 623K is required for complete NCO removal. We will discuss the possible factors that limit NCO oxidation in these surfaces.

9:40am **SS2-TuM6 Kinetics of HCN Decomposition and CNH₂ Formation on Pt(111)**, *X. Hu, M. Trenary, R.J. Meyer*, University of Illinois at Chicago

The kinetics of HCN (hydrogen cyanide) decomposition to H and CN and the subsequent hydrogenation of CN to the CNH₂ species on the Pt(111) surface were studied with time-resolved reflection absorption infrared spectroscopy (RAIRS). The use of RAIRS for kinetic studies can uniquely provide important information on the mechanisms of surface reactions, particularly when these reactions occur below the temperature at which products desorb from the surface. In addition, from the analysis of kinetic data, activation energies for elementary surface reactions on well-defined systems can be determined and thereby provide important experimental benchmarks for comparison with the results of state-of-the-art theoretical calculations. Hydrogen cyanide adsorbs on Pt(111) at a temperature of 85 K to give an intense CH stretch vibration at 3300 cm⁻¹. The time dependent decrease of this peak was monitored at temperatures between 120 and 135 K, the temperature range where the C-H bond of HCN breaks. The decrease in CH stretch peak intensity appears to follow first order kinetics and is attributed to both C-H bond breaking and HCN desorption. The CNH₂ species is characterized by RAIRS peaks at 3370 cm⁻¹ (N-H stretch), 1566 cm⁻¹ (NH₂ scissors), and 1324 cm⁻¹ (C-N stretch). The increase in coverage of the CNH₂ species was monitored by following the time dependence of the 1566 cm⁻¹ peak, the most intense mode of CNH₂, in the temperature range of 210 to 230 K. The CNH₂ formation rate is found to follow second order kinetics. The spectra show the appearance of an intermediate species with a peak at 3347 cm⁻¹, the intensity of which initially increases with time, reaches a maximum, and then decreases as CNH₂ is formed. This peak is identified as the N-H stretch of an HNC surface intermediate. Through kinetic modeling of the time dependence of the coverages of the HCN, HNC, and CNH₂ species, rate constants were derived at each temperature and activation energies were obtained from Arrhenius plots. The experimental results were then compared with the results of density functional theory (DFT) calculations on the stability and structures of the intermediates. Activation barriers for each step of the reaction were also obtained from the DFT calculations. The calculations confirm that CNH₂ is the energetically favored product of the reaction and that CNH₂ has the structure implied by the RAIR spectra. The calculations also predict that HNC is a stable surface intermediate. However, the structures of both adsorbed HCN and HNC as implied from the RAIRS data disagrees with the optimized structures obtained from the DFT calculations.

10:40am **SS2-TuM9 Surface Segregation on Composition Spread Alloy Films**, *A.J. Gellman, J.B. Miller, D. Priyadarshini*, Carnegie Mellon University

Surface segregation has been studied in Pd_xCu_{1-x} alloys used for hydrogen purification membranes. Surface segregation influences the performance of these alloys for hydrogen purification and furthermore, segregation at the surfaces of these materials is a sensitive function of the concentration of contaminants such as sulfur. Segregation is not just restricted to the topmost atomic layer of the alloy. The concentration of one component in the top few layers of the surface may differ from that of the bulk. Because surface segregation is a continuous function of bulk composition, x, a complete understanding of segregation in a binary alloy requires the development of high throughput methods that allow concurrent measurements of surface segregation at all possible values of bulk composition.

Surface segregation has been studied in a Pd₇₀Cu₃₀ alloy using both x-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). The results show that the topmost atomic layer is rich in Cu. On the other hand, the near-surface region consisting of the immediate subsurface layers is rich in Pd. Furthermore, the adsorption of sulfur on the surface causes the complete elimination of Cu from the topmost layer.

A high throughput method for study of surface segregation has been developed that is based on the deposition of thin Composition Spread Alloy Films (CASFs) that contain all possible bulk compositions of the Pd_xCu_{1-x} alloy. Spatially resolved surface analysis of the surface of the Pd_xCu_{1-x} CASF has been achieved using XPS. The results show that the near-surface region of the alloy is Pd rich over a wide range of bulk Pd concentrations.

11:00am **SS2-TuM10 Catalytic Hydrogenation of Butadiene on Bimetallic Surfaces**, *M. Moors, C. Breinlich*, University of Bonn, Germany, *T. Kobiela*, Warsaw University of Technology, Poland, *C. Becker, K. Wandelt*, University of Bonn, Germany

Investigations of bimetallic systems with regard to their surface composition, morphology and adsorption properties for reactive gases are essential for the development of new catalysts with higher efficiency and durability. An interesting catalytic reaction is the partial hydrogenation of butadiene to 1-butene without complete hydrogenation to butane and the coking of the catalyst due to decomposition of the educt. In this work the hydrogenation of butadiene has been investigated on bimetallic Sn-Pd(111) and Au-Pd(111) surface alloys by means of Ultraviolet Photoelectron Spectroscopy (UPS) and Temperature Programmed Desorption (TPD). The bimetallic surfaces were prepared by depositing Sn or Au onto a clean Pd(111) surface followed by controlled annealing. Annealing an at least 4 ML thick Sn film to 750 K results in an ordered p(2x2) Pd₃Sn surface alloy as evidenced by Low Energy Electron Diffraction (LEED). Further annealing to 850 K leads to the formation of the thermodynamically more stable (√3x√3)R30° Pd₂Sn surface alloy. After annealing to 1000 K all Sn has diffused into the Pd(111) substrate. No ordered alloy phase has been found for the Au-Pd system. Annealing to temperatures gradually higher than 450 K leads to a continuous decrease of the Au surface concentration until at 1050 K Au has completely disappeared into the bulk. Under UHV conditions the Sn-Pd(111) alloy surfaces exhibit a lower hydrogenation rate of butadiene in comparison to the pure Pd(111) surface. The butene production strongly decreases with increasing Sn amount at the surface. This decreasing reactivity, however, is accompanied by an increasing selectivity and decreasing coking of the surface. Alloying Pd with Au on the other hand results in a significantly improved reactivity towards butene compared to pure Pd(111), while the selectivity is only slightly decreased. Furthermore, the coking of the Au-Pd(111) surface is even lower than observed on pure Pd(111), which makes this system a promising hydrogenation catalyst.

11:20am **SS2-TuM11 Buffer Layer Assisted Deposition of Pb-Au Bimetallic Nano-clusters: Characterization and Chemical Reactivity**, *M. Asscher*, Hebrew University of Jerusalem, Israel

Control over size and density of metallic nano-particles on oxide surfaces is important for studying model heterogeneous catalysts.

We have deposited metallic clusters on model SiO₂ / Si(100) support, assisted by amorphous solid water (ASW) as a buffer. One may control this way the average size and density of metallic clusters independently by changing the ASW layer thickness, metal dosage and then repeat the deposition process. Bimetallic Pd-Au clusters were prepared this way and characterized by IR spectroscopy, AFM, SEM and TEM measurements in order to determine their structural and crystalline nature.

Directly deposited pure Pd clusters, 5±2 nm diameter, were found reactive in acetylene trimerization to benzene. The buffer assisted Pd-Au bimetallic clusters in comparison, are at least three times more reactive than the pure Pd, in spite of having smaller surface density of Pd atoms. Acetylene hydrogenation to ethylene was also studied. This product is two orders of magnitude more probable than benzene. Once again the bimetallic alloy was

significantly more reactive than the pure Pd. Clean gold clusters were totally inactive. Preliminary results reveal the effect of pre-annealing to temperature below 300K, suggesting strong sensitivity to sintering. The possibility of size dependent reactivity will be discussed.

11:40am **SS2-TuM12 Theoretical Prediction of Ordering and Reactivity of Bimetallic Gold Alloy Surfaces**, *J. Stephens, H. Ham, G. Hwang*, University of Texas at Austin

Bimetallic materials have shown great promise for the development of superior catalysts. The recent surge of new interest in catalysis by gold has led researchers to investigate the effects of adding gold to other metals. While mechanisms underlying the alloying effect are still not understood in detail, recent evidence suggests that the enhanced reactivity of bimetallic catalysts can be attributed to a combination of metal-metal interactions (ligand effect) and unique mixed-metal surface sites (ensemble effect). The ability to accurately predict the arrangements of constituent atoms in a surface alloy is indispensable to unraveling the roles played by the ensemble and ligand effects in the performance of bimetallic model catalysts. We might expect that the arrangement of surface and near-surface atoms is a complex function of temperature, stoichiometric ratio, and surface facet, but thus far, only very limited theoretical effort has been undertaken to determine the atomic distribution of bimetallic alloys. We have developed a scheme to predict the equilibrium arrangement of atoms in surface alloys at finite temperatures. Our scheme is based on the Ising model, and is capable of reproducing DFT-predicted total energies to within no more than a few meV per surface atom. We will present our scheme in detail, as well as what we have learned about the effects of temperature, composition, surface facet, and particle identity on the arrangement of surface atoms for various gold-based binary alloys including gold-palladium and gold-platinum. We will also discuss how the atomic arrangements affect the reactivity of gold-based alloy surfaces particularly towards oxidation of hydrogen and carbon monoxide.

Tuesday Afternoon, November 10, 2009

Surface Science

Room: C1 - Session SS1+PS+TF+AS+NS-TuA

Non-Thermal Chemistry / Ion, Electron Processes

Moderator: A.V. Walker, University of Texas at Dallas

2:00pm **SS1+PS+TF+AS+NS-TuA1 Growth and Purification of Nanostructures Deposited by Electron Beam Irradiation: A Surface Science Perspective**, *H. Fairbrother, J. Wnuk, J. Gorham, S. Rosenberg*, Johns Hopkins University, *T. Madey*, Rutgers, *W.F. van Dorp, K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam induced processing (FEBIP) of volatile organometallic precursors has emerged as an effective and versatile method of fabricating metal-containing nanostructures. However, to improve the materials properties of FEBIP nanostructures, provide information that can aid in the rational design of new precursors and improve the modeling of the FEBIP process it is necessary to better understand the molecular level processes associated with the electron stimulated decomposition of organometallic precursors. To address this issue, we have employed a UHV-surface science approach to study the electron induced reactions of dimethyl(acetylacetonate) gold(III) ($\text{Au}(\text{acac})\text{Me}_2$), a common precursor used for Au deposition in FEBIP, adsorbed on solid substrates. Surface reactions, reaction kinetics and gas phase products were studied using incident electrons in the energy regime between 40-1500 eV, using a combination of XPS, RAIRS and MS. XPS data indicate that electron irradiation of $\text{Au}^{\text{III}}(\text{acac})\text{Me}_2$ is accompanied by the reduction of Au^{III} to a metallic Au^0 species embedded in a carbon matrix while MS reveals the concomitant evolution of methane, ethane and hydrogen. The electron stimulated decomposition of the $\text{Au}^{\text{III}}(\text{acac})\text{Me}_2$ precursor can be described by a first-order decay process with respect to the surface coverage, with a rate constant that is proportional to the electron flux and a total reaction cross-section of $\approx 3.6 \times 10^{-16} \text{ cm}^2$ at an incident electron energy of 520 eV. As a function of the incident electron energy, the maximum deposition yield was observed at ≈ 175 eV. Our results are consistent with the idea that those carbon atoms removed as volatile species from the $\text{Au}^{\text{III}}(\text{acac})\text{Me}_2$ precursor during FEBIP are associated with methyl groups attached to the central Au atom. In related studies we also studied the effects of atomic oxygen and atomic hydrogen on Au-containing carbonaceous films deposited by electron beam irradiation of $\text{Au}(\text{acac})\text{Me}_2$, as a potential route to purify FEBIP deposits. Atomic oxygen was found to be the more effective of the two radical treatments in removing carbon, although a surface layer of gold oxide was formed. Subsequent exposure of this overlayer to atomic hydrogen rapidly removed the oxide, resulting in a pure Au film. AFM analysis of FEBIP deposits before and after radical treatment support the idea that carbon abatement is accompanied by a decrease in particle size.

2:20pm **SS1+PS+TF+AS+NS-TuA2 Surface Morphology Control and 3D Structure Development with Cryogenic Assisted Electron Beam-Induced-Deposition**, *M. Bresin, K.A. Dunn*, University at Albany SUNY

Electron beam-induced-deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID. 3D structures were developed using a multilayer deposition method, facilitating the creation of hanging, suspended or incorporated-gap structures.

Experiments were performed using an FEI Nova 600 Nanolab dual beam system with a LN2 cryogenic stage, enabling substrate temperatures of -155 ± 5 °C. A gaseous platinum precursor (MeCpPtMe_3) was first condensed onto the cooled substrate using a capillary-style gas injection system (GIS). Condensate thicknesses between 100nm-3mm were produced by adjusting the GIS-substrate gap and precursor crucible temperature. Next, gas flow was terminated and the condensate was irradiated with an electron beam to induce precursor decomposition. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions showed clear evidence of successful deposition. The morphology of the deposited material depended on exact deposition conditions, and exhibited several distinct types absent from deposits made by conventional (room temperature) EBID.

3D structures were developed with a multilayer deposition method. In this method, multiple layers were used to take advantage of the electron penetration depth within the condensate, through which the depth of

deposition could be controlled. An initial layer was first condensed and a region was deposited with the electron beam to act as a substrate-anchoring site. A second condensed layer was then applied such that electrons could only penetrate to the top of the initial condensed layer. The electron beam was then shifted, to deposit a section partially over the anchoring region (in the initial layer) with the remainder over unreacted area. After reheating, part of the second deposit was found to have adhered to the anchoring region, while the rest hung over vacuum. Using similar process, structures were also developed to create embedded gaps or tunnels.

Taken together, these observations have important implications for the creation of arbitrarily large or complex structures previously untenable by EBID fabrication. The growth mechanism and potential applications will be discussed, from nanotechnology to osteointegration.

2:40pm **SS1+PS+TF+AS+NS-TuA3 Nanoscale Patterning and Graphene Film Deposition on Si using Low-energy Electron Beams**, *T.M. Orlando, D. Sokolov, D. Oh, K. Shepperd*, Georgia Institute of Technology

INVITED

The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for many electron-beam induced processes in materials growth, etching, and lithography. We have demonstrated experimentally and theoretically that the total ESD yield of adsorbates can be a function of the incident low-energy electron-beam direction. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). We have also explored three graphene growth strategies which utilize low-energy electron beams and non-thermal reactions. The first uses electron beam irradiation in conjunction with chemical vapor deposition techniques to grow graphene directly on Si substrates. This approach utilizes unsaturated hydrocarbon precursor molecules and can be carried out at relatively low temperatures. The second involves electron-stimulated removal of oxygen and organic fragments from graphene-oxide flakes positioned on patterned Si substrates. This may allow for damage-free reduction of graphene-oxide to graphene. The third involves electron-beam removal of defects from graphene epitaxially grown from SiC(0001) substrates.

4:00pm **SS1+PS+TF+AS+NS-TuA7 A Study of the Nucleation of Focused Electron Beam Induced Deposits: Growth Behavior on the Nanometer Scale**, *W.F. van Dorp*, Delft University of Technology, The Netherlands, *J.B. Wagner, T.W. Hansen, R.E. Dunin-Borkowski*, Danish Technical University, Denmark, *K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam-induced deposition (FEBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled nearly to the level of single molecules. Currently, the highest resolution that is reported is 0.7 nm [1] using the precursor $\text{W}(\text{CO})_6$. At this scale, deposits contain no more than a few molecules on average. Our ultimate goal is to develop the ability to deposit single precursor molecules in a consistent manner.

We perform our FEBID experiments in environmental scanning transmission electron microscopes (E-STEM) with a beam energy of 200 keV and a 0.2 nm probe. The annular dark field (ADF) signal is used for the imaging of the deposits. By recording the ADF signal during deposit growth we are able to monitor the growth process in situ. Thin, electron transparent graphite is used as a substrate and typical precursor gas pressures at the sample during the deposition were 10^{-3} to 10^{-5} Torr.

In the present study we used Me_3PtMeCp , a Pt-precursor that is often used in FEBID experiments [2]. To improve on the currently achieved resolution, it is important to study the nucleation stage of deposits. When using a graphite substrate we found that there is a significance difference in deposition behavior between the $\text{W}(\text{CO})_6$ and Me_3PtMeCp precursors. Where the typical growth behavior for $\text{W}(\text{CO})_6$ is to form nm-sized or even sub-nm sized deposits, the deposits fabricated from Me_3PtMeCp are a few nanometers in diameter and consist of individual sub-nm sized grains. We report on our study of this difference in growth behavior and strategies to increase the writing resolution.

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruij, Nanotechnology 19 (2008) 225305

[2] A. Botman, M. Hesselberth, J.J.L. Mulders, Microelectron Eng 85 (2008) 1139

4:20pm **SS1+PS+TF+AS+NS-TuA8 Direct Local Deposition of High-Purity Pt Nanostructures by Combining EBID and ALD**, *A.J.M. Mackus*, Eindhoven University of Technology, the Netherlands, *H.J.J.L. Mulders*, *A.F. de Jong*, FEI Electron Optics, the Netherlands, *M.C.M. van de Sanden*, *W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions electron beam induced deposition (EBID) has the potential to become a key nanomanufacturing technology. The technique suffers however from incomplete decomposition of the precursor gas and consequently a low material purity. Platinum EBID yields typically only a purity of ~15 at.% and a resistivity value orders of magnitude higher than bulk resistivity which reduces the functionality of the material for most nanoprotyotyping applications such as adding electrical contacts to nanodevices. In this contribution we propose a novel approach for the fabrication of high-purity Pt nanostructures based on a combination of the patterning capability of EBID and the high material quality obtained by atomic layer deposition (ALD). The latter technique yields submonolayer control of the film thickness and in the case of Pt ALD high purity (~100%), low resistivity ($13 \pm 1 \mu\Omega\text{cm}$) films [1]. The developed approach comprises seed layer deposition by EBID and area-selective ALD growth. For specific conditions the thermal ALD process of Pt (MeCpPtMe₃ precursor, O₂ gas) was found to start selectively on an EBID seed layer with a thickness equivalent to one monolayer Pt. It was established that the deposits have a uniform thickness and a high purity value (>93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. In addition to the approach and the material properties the underlying reaction mechanism of the (area-selective) Pt ALD process will be discussed, including aspects such as the role of dissociative chemisorption of O₂ molecules on Pt and the formation of H₂O, CO₂, and CH₄, reaction products.

[1] H.C.M. Knoop, A.J.M. Mackus, M.E. Donders, M.C.M. van de Sanden, P.H.L. Notten, and W.M.M. Kessels, *Electrochem. Solid-State Lett.* **12**, G34 (2009)

4:40pm **SS1+PS+TF+AS+NS-TuA9 Anionic Surface Processes Induced by Low-Energy Electrons**, *P.A. Rowntree*, University of Guelph, Canada **INVITED**

The historical development of surface chemistry has largely been based on the use of free-energy-driven processes; an enormous volume of literature exists that details the search for chemical control over these processes using the classical parameters of temperature, surface composition and reagents. However, as the interest in controlling the processes grows, and the need to produce structurally resolved reactive systems increases, alternative non-thermal mechanisms are increasingly being explored in order to drive the interfacial processes into reaction channels chosen by the needs of the operator instead of the principles of thermochemistry. Our specific interest is in the control of surface processes using low-energy electrons as speciality 'reagents' that can be delivered to surfaces in a highly controlled manner, and interact with surface species according to understandable and reproducible mechanisms. The overall goal is to understand and manipulate these mechanisms to selectively interact with target molecules of our choosing to modify surfaces according to our needs.

This presentation will focus on two aspects of this 'manipulative' approach to surface chemistry. The first is our recent development of ways to selectively control where incident electrons interact with the organic monolayers that are deposited on Au(111) surfaces. These chemically homogeneous monolayers have a highly uniform electronic structure along the length of the chains, such that it is normally not possible to strongly enhance the dissociation probabilities at any given site. We have found that it is possible to selectively enhance the rupture of C-H bonds at the methyl terminations of these films by coupling the incident electron flux with anionic excitonic states of rare gas solids that are adsorbed on these methyl terminations. The energy+charge transfer process that leads to bond rupture is extremely sensitive to the incident energy as well as the chemical nature of the target species, thus enhancing the selectivity of the local modifications to the organic surface. A second set of processes will be discussed that involves the electron-induced decarbonylation of metal carbonyls adsorbed on organic surfaces to produce atomic metal deposits. We have shown that low-energy electrons can induce surface polymerization reactions in Fe(CO)₅ films that lead to apparent CO-elimination cross-sections greater than 1 nm². This strong coupling to dissociative processes allows us to develop thin metal overlayers without the substrate damage that is usually associated with using thermal evaporation or sputtering processes.

5:20pm **SS1+PS+TF+AS+NS-TuA11 Condensed Phase Electron-Stimulated Reactions: Desorbed Anions and Retained Radicals**, *Y. Shyur*, *J. Wang*, *S. Lau*, *E. Krupczak*, *C. Arumainayagam*, Wellesley College

Studies of low-energy electron-induced processes in nanoscale thin films serve to elucidate the pivotal role that low-energy electron-induced reactions play in high-energy radiation-induced chemical reactions in condensed matter. While electron-stimulated desorption (ESD) experiments conducted during irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products following low-energy electron irradiation can provide new insights into radiation chemistry. We have used post-irradiation temperature-programmed desorption to identify labile radiolysis products as demonstrated by the first identification of methoxymethanol as a reaction product of methanol (CH₃OH) radiolysis. Although low-energy electron-induced oligomerization reactions have been previously reported for molecules such as thiophene and cyclopropane, our electron-induced studies of CCl₄ represent the first study to specifically identify the products of such reactions, demonstrating the utility of post-irradiation temperature programmed desorption experiments to study the radiation chemistry of condensed matter. Results of post-irradiation studies have been used not only to determine the identity of radiolysis products, but also to determine the dynamics of electron-induced reactions. By comparing our post-irradiation results to previous electron stimulated desorption studies of anion production during irradiation of condensed CF₂Cl₂ and CF₃I, we examine the relationship between desorbed anions and retained radicals during dissociative electron attachment in the condensed phase.

5:40pm **SS1+PS+TF+AS+NS-TuA12 Cluster-induced Desorption and Ionization of Biomolecules for Application in Mass Spectrometry**, *M. Dürr*, Hochschule Esslingen, Germany, *C. Gebhardt*, *A. Tomsic*, *H. Schröder*, *K. Kompa*, MPI für Quantenoptik, Germany

Mass spectrometry of biological macromolecules has developed into a key technology for fast routine analysis in biotechnology. A critical issue is the efficient transfer of non-volatile biomolecules out of their sample solution into the gas phase in combination with their concomitant ionization. Here we show that a beam of neutral molecular clusters consisting of 10³ to 10⁴ SO₂ molecules can be used for the desorption and ionization of biomolecules. Cluster impact on arbitrary surfaces pre-treated with biomolecules efficiently creates cold, desolvated, gas phase biomolecular ions as large as 6000 u without any need for preparation of the biomolecules in a special matrix or post-ionization after desorption. Since the cluster provides not only the energy for the desorption process but also a transient matrix during the process, the molecules are found to be desorbed without any fragmentation.

As revealed by means of molecular dynamics simulations, high kinetic temperatures in the order of a few thousand Kelvin are reached during cluster impact on the surface. However, these extreme conditions prevail only for some picoseconds, since shattering of the initial cluster leads to very fast energy dissipation. Already after 20 ps, the SO₂ cluster fragments have reached a temperature colder than the original temperature of the adsorbates. This fast energy dissipation excludes efficient energy transfer into the vibrational degrees of freedom relevant for the cleavage of the relatively large biomolecules and thus allows for their soft, fragmentation-free desorption.

Surface Science

Room: M - Session SS2-TuA

Wide Band Gap Semiconductors

Moderator: V. Bermudez, Naval Research Laboratory

2:00pm **SS2-TuA1 The Functionalization of Semiconductor Surfaces with Hemin**, *M. Losurdo*, IMIP-CNR, Italy, *S.D. Wolter*, Duke University, *M. Giangregorio*, IMIP-CNR, Italy, *T.H. Kim*, Duke University, *G.V. Bianco*, *P. Capezzuto*, *G. Bruno*, IMIP-CNR, Italy, *A.S. Brown*, Duke University

Selective and sensitive detection of Nitric Oxide (NO) with a device that will monitor its concentration continuously for biological, environmental, and defense applications is highly desirable. One method of accomplishing this detection, is to functionalize a semiconductor surface with metaloporphyrin groups. Specific metaloporphyrins may be chosen for analyte selectivity. Heme, Fe-Protoporphyirin IX (hemin), for example, binds NO with much greater affinity, than to other gases such as O₂ and CO.

Herein, we present and discuss the semiconductor surface and interface chemistry involved in the chemisorption of hemin on III-V surfaces

including InP, GaAs, GaN and on group-IV semiconductors including SiC and Si.

The peculiarity of our study is the use of spectroscopic ellipsometry for the monitoring of surface coverage and interface phenomena. Ellipsometry data are corroborated by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and electrical force microscopy. We discuss the dependence of semiconductor surface treatments e.g. native oxide, chemical treatments, passivating processes whose role is pre-conditioning the surface with $-H$ or $-NH$ terminal groups) on the self-assembling of the functionalizing biomolecules, and of the concentration of the hemin solution and chemistry duration on the chemistry and kinetics of the various semiconductor functionalization. We report also on the effect of benzoic acid addition to the hemin solution as a spacer to prevent formation of hemin aggregates in favor of normal-to-surface hemin orientation. By investigating a number of semiconductor base systems with a gap ranging in a broad range from 0.4 eV (InAs) to 3.4 eV (GaN) we demonstrate for the first time the correlation existing between the sensing activity and the semiconductor gap. This correlation might be useful to choose the appropriate semiconductor-based platform for a target sensing application. A correlation between the band gap of the semiconductors, the surface binding sites and the efficacy of functionalization is established and discussed.

This work is supported by the 7FP European Project NanoCharM (Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry)

2:20pm SS2-TuA2 Photoelectrochemical Etching of a Non-Polar GaN LED. *H.-Y. Kim*, Korea University, South Korea, *M.A. Mastro, C.R. Eddy, Jr.*, US Naval Research Laboratory, *J. Kim*, Korea University, South Korea
Light emitting diode (LED) structures fabricated from GaN-based material grown from along the polar c -axis possess a large polarization field within the active quantum well that hampers the efficiency of the device. This internal electric field separates the electrons and holes, which reduces the recombination rate in the quantum well (QW). To improve the light emission efficiency, we fabricated QW-LEDs from GaN-based material grown in the non-polar a -plane on r -plane sapphire. Implementing this approach to enhance the internal quantum efficiency on commercially available 2-inch r -plane sapphire required the development of a medium temperature AlN/GaN buffer layer scheme. Not only improved internal efficiency but also improved external efficiency is required to achieve high brightness LEDs. To date, the only widely applied technique to enhance the extraction of light from commercial polar GaN LEDs is to roughen the surface by dry or wet etching. We developed a photoelectrochemical (PEC) etching approach for the a -plane non-polar GaN LED. The samples were dipped into the KOH solution and exposed to UV light generated from a mercury lamp. A detailed investigation was conducted into the effect KOH concentration as well as the intensity of UV exposure on the etch rate and morphology of the surface. The PEC etching of the asymmetric bond structure along the $[0001]$ and $[1-100]$ directions generated the elongated dimples and roof-shape pillars. The density of the pillars and the width of the dimples increased with increased etching time. The dimples and pillars (surface texturing) on the surface provides an ensemble of angles for light to escape that is normally trapped within the crystal. Photoluminescence measurements were conducted to investigate the relationship between extraction efficiency and surface texturing by this PEC etching technique.

2:40pm SS2-TuA3 Surface Photovoltage and Band Bending in GaN. *A.A. Baski, M.A. Foussekis, M.A. Reshchikov*, Virginia Commonwealth University

INVITED

Although GaN is a wide-band gap semiconductor being successfully utilized in high-temperature and optoelectronic devices, the influence of surface effects such as band bending on the electrical and optical properties of GaN is not yet well understood. It is known that negative surface charge on air-exposed, undoped n -type GaN causes a substantial upward band bending of 0.4 – 1.5 eV. This band bending can be reduced by 0.3 to 0.9 eV during UV illumination, known as surface photovoltage (SPV), due to the accumulation of photo-generated holes at the surface. We have investigated the dependence of the SPV on illumination intensity and wavelength, as well as its transients after turning on and off illumination, using a Kelvin probe mounted in an optical cryostat. As expected, the initial SPV rise is slow at low illumination intensities and fast at higher intensities, where its initial slope is a linear function of illumination intensity. The SPV signal in air ambient under UV illumination increases within seconds to a maximum (0.4 to 0.7 V), but then gradually decreases during illumination. A similar behavior occurs in an oxygen environment (but not nitrogen), indicating that surface oxygen species are the primary component responsible for the observed SPV decrease. In vacuum, the SPV signal quickly increases but then slowly increases under UV illumination. This SPV behavior is consistent with the photo-induced adsorption of negatively charged oxygen species in air and their desorption in vacuum. After ceasing illumination,

the SPV decays nearly logarithmically regardless of environment, but requires substantially longer to reach its dark value after extended illumination in vacuum.

We explain the transient and steady-state SPV under UV illumination using both internal and external mechanisms. The internal mechanism involves photogenerated holes that accumulate at surface states and recombine with free electrons from the bulk, whereas the external mechanism involves electrons that tunnel through a thin oxide layer and are captured by surface species, resulting in chemisorption. Our proposed phenomenological model quantitatively explains SPV data for low intensity UV light using only the internal mechanism; however, illumination at high intensities requires the inclusion of photo-induced chemisorption or desorption processes. Our studies to date have focused on n -type GaN, but we have preliminary data for p -type GaN indicating an initial downward band bending of ~ 1 eV and an unexpected increase in band bending under UV illumination. Studies of the band bending and SPV transients in different ambients are in progress and will be reported as well.

4:00pm SS2-TuA7 Adsorption Processes on Silicon Carbide Surfaces. *J. Pollmann*, Universitaet Muenster, Germany

INVITED

Many experimental and theoretical studies of adsorption processes on semiconductors have employed Si(001) as a prototype substrate surface. The ionic group IV compound semiconductor silicon carbide (SiC), which is of large fundamental interest and of high application potential for electronic devices and sensors, offers particularly interesting new degrees of freedom for adsorption because of its different lattice constant and its rich variety of surface reconstructions giving rise to very amazing adsorption behaviour. For example, molecular hydrogen adsorbs dissociatively on SiC(001)- $c(4 \times 2)$ while it does not adsorb on SiC(001)- (3×2) at room temperature although both surfaces are characterized by similar surface dimers. Likewise the covalent attachment of organic layers to the SiC(001)- (3×2) surface, contrary to the Si(001)- (2×1) surface, gives rise to structurally well-defined configurations that can play a key role in organic functionalization. Incorporating new functionalities at SiC surfaces by adsorption of hydrogen or hydrocarbons requires a detailed understanding of the adsorbate-surface structure and its properties. In this talk adsorption of hydrogen, acetylene, ethylene and benzene on SiC(001) surfaces will be discussed. Scrutinizing a number of conceivable reaction scenarios within first-principles theory allows us to follow surface reactions on a microscopic level giving access to reaction mechanisms, transition states, barrier heights and adsorption energies and thus to identify the physical origin and nature of the peculiar adsorption behavior of SiC(001) surfaces. The theoretical results will be reviewed and discussed in comparison with available experimental data, as well as results for related adsorption processes on the Si(001)- (2×1) surface.

5:00pm SS2-TuA10 Temperature Stabilised Surface Reconstructions in Humid Atmospheres and pH-dependent Stabilization Mechanism at Polar ZnO(0001) -Zn Surfaces. *M. Valtiner, M. Todorova, J. Neugebauer*, Max-Planck-Institute für Eisenforschung GmbH, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry of oxides in humid atmospheres and in water based electrolytes (as e.g. oxide dissolution promoting effects of H^+ and OH^-) is an important aspect of molecular adhesion and related phenomena. Preparation and characterization of atomically well-defined oxide/electrolyte model interfaces, which allow well-defined molecular adhesion studies, are the most challenging issue in this context. Therefore, this contribution will focus on experimental results of the preparation of single crystalline ZnO(0001)-Zn model surfaces in humid atmospheres and complementary DFT-based ab-initio thermodynamics studies.

The main focus is the preparation and characterisation of surfaces, which are well defined on an atomic scale. The atomic structure of the polar ZnO(0001) surfaces in dry and humid oxygen environment was studied by diffraction experiments and density-functional theory in combination with atomistic thermodynamics. Our results indicate that for similar stoichiometries a large number of very different, but energetically almost degenerate reconstructions exist. Thus vibrational entropy, which could be safely neglected for most semi-conductor surfaces, becomes dominant giving rise to a hitherto not reported strong dependence of surface phase diagrams on temperature. Based on this insight we are able to consistently describe and explain the experimentally observed surface structures on polar ZnO(0001) surfaces [1,2].

Moreover, it will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline within a wide pH range. An in-situ AFM study of the acidic dissolution allowed an nanoscale imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported on a nanoscopic level [3]. Finally, first results of combining single molecule adhesion measurements with these single crystalline substrates will be highlighted.

[1] M. Valtiner, S. Borodin, G. Grundmeier; *Physical Chemistry Chemical Physics*, 9(19), (2007) 2406-2412.

[2] M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer; submitted to *Physical Review Letters*.

[3] M. Valtiner, S. Borodin, G. Grundmeier; *Langmuir*, 24(10), (2008) 5350-5358.

5:20pm **SS2-TuA11 Electronic Structure of Zinc and Free-Base Tetraphenylporphyrin Derivatives Adsorbed on TiO₂(110) and ZnO(11-20) Surfaces for Application in Dye Sensitized Solar Cells**, S. Katalinic, S. Rangan, R. Thorpe, R.A. Bartynski, J. Rochford, K. Chitre, E. Galoppini, Rutgers University

Metalloporphyrins play an essential role in photosynthetic mechanisms and therefore are natural candidates for electron transfer mediator in dye sensitized solar cells (DSSCs). Among the possible metalloporphyrins, the zinc tetraphenylporphyrins (ZnTPP) derivatives have been found to have similar electron injection and charge recombination properties as the important standard ruthenium dye N3 for DSSCs, as well as reasonable performances using TiO₂ or ZnO as substrates.

Due to a strong decoupling of the meso-phenyls from the main porphyrin macrocycle, the optical absorption properties of the ZnTPP derivatives are found relatively insensitive to the meso-phenyls functionalization. As a consequence, the adsorption geometry on the surface, as well as the molecule-molecule interaction, can be altered independently of the absorption properties.

Using direct and inverse photoemission spectroscopy we have measured the occupied and unoccupied electronic states of several zinc (and free-base for comparison) tetraphenylporphyrin derivatives adsorbed on single crystals TiO₂ and ZnO surfaces. From this, the alignment of the molecular levels (in particular the frontier orbitals) with respect to the substrate band edges can be directly determined. For a full interpretation of the electronic structure of such molecular adsorbates, we have compared our measurements to ab-initio calculations of the density of states. In addition to spectroscopic surface averaged probes, we have used scanning tunneling microscopy to study the local bonding geometries at the surface of the semiconductors. Recent results will be presented and compared to those available in the literature.

Surface Science

Room: N - Session SS3-TuA

Catalysis: Mechanisms & Morphology

Moderator: B.R. Cuenya, University of Central Florida

2:00pm **SS3-TuA1 High Catalytic Activity of CeO_x/Au(111) and Au/CeO_x/TiO₂(110): Special Properties of CeO_x Nanoparticles**, J.A. Rodriguez, J.B. Park, J. Graciani, Brookhaven National Laboratory, J. Evans, Universidad Central de Venezuela, D.J. Stacchiola, S.J. Ma, P.J. Liu, Brookhaven National Laboratory, J. Fdez-Sanz, Universidad de Sevilla, Spain, J. Hrbek, Brookhaven National Laboratory **INVITED**

This talk will focus on a series of studies investigating the catalytic activity of CeO_x/Au(111) and Au/CeO_x/TiO₂(110) for the water-gas shift (WGS, CO + H₂O → H₂ + CO₂) reaction and CO oxidation. Au(111) is inactive for the WGS. The deposition of ceria nanoparticles on Au(111) produces a highly active WGS catalysts. An even better catalysts is produced after depositing Au and CeO_x nanoparticles on TiO₂(110). The titania substrate imposes non-typical coordination modes on the ceria nanoparticles. In the CeO_x/TiO₂(110) systems, the Ce cations adopt an structural geometry and an oxidation state (+3) which are quite different from those seen in bulk ceria or for ceria nanoparticles deposited on metal substrates. The increase in the stability of the Ce³⁺ oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles. The co-deposition of ceria and gold nanoparticles on a TiO₂(110) substrate generates catalysts with an extremely high activity for the production of hydrogen through the WGS or for the oxidation of carbon monoxide. The exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of unconventional surface structures with special chemical activity.

2:40pm **SS3-TuA3 Kinetics and Elementary Steps of the Reverse Water-Gas Shift Reaction over Pt Catalysts**, L.G. Cameron, C.T. Campbell, University of Washington, L. Grabow, M. Mavrikakis, University of Wisconsin

The kinetics of the reverse water gas shift (RWGS) reaction (CO₂ + H₂ → CO + H₂O) have been measured over clean and annealed Pt powder at a variety of conditions, and the surface coverage of adsorbed intermediates

was verified by transient techniques. Under conditions where the surface coverage is very low and the reaction is occurring on essentially adsorbate-free Pt, the RWGS rate is 1000-fold faster than the rate of dissociative CO₂ adsorption (CO₂ → CO + O_{ad}), estimated from measurements of the reverse rate and equilibrium constant for this elementary step. This proves that the dominant mechanism for the RWGS reaction is not via dissociative CO₂ adsorption. The energetics estimated from DFT calculations of potential alternate pathways on Pt(111) suggests that CO₂ is instead activated by reaction with H_{ad} to make a COOH_{ad} intermediate, which dissociates to make CO_{ad} and OH_{ad}. A microkinetic model based on these DFT energetics reproduces well the measured absolute rate per Pt atom, its activation energy, and its dependences on CO₂ and H₂ partial pressures. This offers strong support for this alternate "carboxylate" pathway as dominating the mechanism. Estimates of the degrees of rate control of this reaction's elementary steps and intermediates will also be discussed.

Work supported by DOE-OBES Chemical Sciences Division.

3:00pm **SS3-TuA4 A DFT Study of Methanol Synthesis by CO₂ Hydrogenation on Cu Nanoparticles and Surfaces**, Y. Yang, SUNY at Stony Brook, P.J. Liu, M. White, Brookhaven National Laboratory

The synthesis of methanol from CO₂ and H₂ (CO₂+3H₂→CH₃OH+H₂O) has attracted considerable attention. It is not only environmentally important due to its application in the conversion of greenhouse gas, CO₂, it is also of great industrial significance because the product, methanol, can serve as a raw material for the synthesis of other organic compounds, besides being used as a liquid fuel. Commercially, the reaction is performed on a catalyst containing Cu, ZnO and Al₂O₃ at a high temperature (220-240°C) and high pressure (50-100 bar). There is a need to understand the reaction mechanism in order to develop more active and selective catalysts even though the mechanism is still controversial. In this study, density functional theory (DFT) was employed to elucidate the reaction mechanism on the Cu(111) surface and the promotion effect of nano-size Cu compared to bulk Cu.

Cu₂₉ nanoparticles, exposing a combination of (100) and (111) faces in a pyramidal structure, is the model we used to study the reaction pathways on the Cu nanoparticles. For comparison, the reaction mechanism on the Cu(111) surface is also studied. It was found out that on both systems, the reaction undergoes via formate (HCOO) and dioxomethylene (H₂COO). The reaction rate is controlled by hydrogenation of HCOO and H₂COO. In accordance with experimental findings, our results show that the Cu₂₉ nanoparticles display a superior activity over Cu(111). The better behavior of Cu₂₉ is associated with the low-coordinated Cu sites, which provide a reasonably strong binding to the intermediates.

v

4:00pm **SS3-TuA7 Electronic Structure Effect in Modified Reactivity of Pt/Cu(111)**, T. Anniyev, S. Kaya, H. Ogasawara, Stanford Synchrotron Radiation Lightsource, S. Koh, P. Strasser, University of Houston, M. Toney, A. Nilsson, Stanford Synchrotron Radiation Lightsource

A key role in the activity of transition metal catalysts is the degree of interaction of metal d-bands with the adsorbed atoms/molecules [1]. It has been suggested that d-band center is a single effective measure of this interaction [2]. In this work we demonstrate how strain induced electronic structure changes can be used to tune the catalytic activity of the Oxygen Reduction Reaction (ORR). The limiting factor in the performance of the Pt-based PEM fuel cells is the low rate of the ORR taking place at the cathode. It has recently been shown that electrochemically leached PtCu catalysts, which have strained Pt rich shell due to dissolution of Cu, exhibit uniquely high reactivity for this reaction [3]. Using a surface science approach we have investigated the electronic structure effect in the enhanced ORR activity using Pt monolayers epitaxially grown on Cu(111) as a model system. We show that compressive strain and host substrate-induced changes in the Pt d-band center are responsible for the changes in chemisorption strength of adsorbed oxygen. Electronic nature of chemisorbed oxygen atoms on strained Pt monolayers has been investigated by probing oxygen projected density of states below and above the Fermi level using X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS), respectively. Combined oxygen K-edge XAS and XES results of oxygen on strained Pt monolayers show lowering of the adsorbate projected density of states and a complete filling up of antibonding states above Fermi level indicative of weakened metal-oxygen bond relative to that of oxygen on Pt(111). The weakening of the metal-oxygen bond is correlated with the broadening and lowering of the Pt d-band probed by valence band X-ray photoemission spectroscopy (XPS). The observed results are explained in terms of the d-band model.

References

[1] B. Hammer and J. K. Nørskov, *Theoretical surface science and catalysis—calculations and concepts*, Adv. Catal. 45, 71 (2000).

[2] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis (John Wiley & Sons, New York, 1994).

[3] S. Koh and P. Strasser, Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface de-alloying, *J. Am. Chem. Soc.*, 129 (42), 12624-12625 (2007).

4:20pm **SS3-TuA8 In Situ Study of Heterogeneous Catalysis on Oxide Support: CO Oxidation on Au/TiO₂ Catalysts**, *S. Porsgaard*, Lawrence Berkeley National Lab and University of Aarhus, Denmark, *P. Jiang*, *F. Borondics*, *M. Köber*, Lawrence Berkeley National Lab, *S. Wendt*, University of Aarhus, Denmark, *H. Bluhm*, Lawrence Berkeley National Lab, *F. Besenbacher*, University of Aarhus, Denmark, *M. Salmeron*, Lawrence Berkeley National Lab

It has been known for more than a decade that the system of gold nanoparticles on a TiO₂ support (Au/TiO₂) is an active catalyst for a variety of reactions even below room temperature.[1] However, there is still little agreement on several important questions such as the role of the substrate, the charge state of gold, and the role of oxygen vacancies, even for the simplest reaction of CO oxidation.

In this study we focus on the questions related to the electronic band structure of the substrate. We chose a model system of evaporated Au nanoparticles on a rutile TiO₂(110) single crystal substrate. The morphology of the evaporated Au nanoparticles were studied by STM, and it turned out to be strongly dependent on the pre-treatment of the TiO₂ surface.[2]

For traditional surface science, the pressure gap between the studies in ultra high vacuum (UHV) and the industrial relevant reaction conditions is an important challenge. To overcome this problem, we have used in situ X-ray Photoelectron Spectroscopy (in situ XPS)[3] to study the evolution of the adsorbed chemical species and the electronic band structure of the rutile TiO₂(110) during the individual steps in the reaction under pressures up to 1 Torr.

However, XPS on semiconductor substrates is challenging especially in the presence of gases. We have designed novel samples and test experiments to overcome these drawbacks. These results show that most in situ experiments on semiconductor substrates require extraordinary precautions. Now, we are able to avoid the newly discovered pitfalls, and we are able to present decisive results on the previously debated problems, e.g. the ongoing discussion about the charge state of gold and the role of oxygen vacancies.

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4:40pm **SS3-TuA9 Search for Chemicurrent during CO Oxidation on Pt/GaN and Pt/TiO₂ Nanodiodes**, *J.R. Creighton*, *E.J. Heller*, *K.H.A. Bogart*, *M.E. Coltrin*, *E.N. Coker*, *K.C. Cross*, Sandia National Laboratories
In 2005, Gabor Somorjai's group demonstrated the capture of chemical energy liberated during carbon monoxide oxidation on Pt and Pd surfaces by using a structure they described as a "catalytic nanodiode" [1-2]. This device is a Schottky diode where the metal contact is made of an ultrathin (~5 nm) catalytic metal, deposited on a wide bandgap semiconductor such as GaN or TiO₂. During the exothermic oxidation of CO, some fraction of the chemical energy may be dissipated by creation of hot electrons in the catalytic metal, and some of these electrons are potentially collected on the semiconductor side of the Schottky barrier. In principle, this "chemicurrent" formed by hot electron generation, transport, and collection represents the conversion of chemical energy directly into electrical energy. For some conditions using a Pt/TiO₂ nanodiode, a remarkable conversion efficiency of 3 electrons per 4 CO₂ produced was measured [1]. We have fabricated several versions of catalytic nanodiodes using GaN and TiO₂ films deposited and characterized in-house. During CO oxidation on Pt/GaN and Pt/TiO₂ nanodiodes we also detect a current that is unambiguously a result of the chemical reaction. We measure current densities up to 100 nA/mm² and reaction conversion efficiencies in the range of 10⁻⁵-10⁻³ electrons per CO₂, which are quantitatively similar to reports in more recent publications [3-4]. However, the behavior of this chemical signal as a function of diode impedance indicates that it is derived from a **voltage source**, and not from a current source. In fact, the chemical signal is primarily, if not entirely, due

to the thermoelectric voltage generated and/or modified by the exothermicity of the reaction. We have yet to find any conclusive evidence supporting true "chemicurrent" formation during CO oxidation on Pt/GaN or Pt/TiO₂ nanodiodes.

References:

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5:00pm **SS3-TuA10 MORTON S. TRAUM AWARD FINALIST: Morphology and Chemical Reactivity of Bi-Metallic Au-Pd Clusters**, *E. Gross**, *M. Asscher*, The Hebrew University of Jerusalem, Israel

Bi-metallic clusters have unique catalytic properties, since one metal can modify the electronic and thus the catalytic properties of the other metal. Here we describe a unique preparation method of bimetallic Pd-Au nanoclusters. The growth mode is based on initial evaporation of metal atoms on top of amorphous solid water adsorbed on SiO₂/Si(100) substrate at 100K under ultra high vacuum (UHV) conditions. The ice buffer layer separates the small metallic seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth of nano-clusters in a Buffer Layer Assisted Growth (BLAG) mechanism.

Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) measurements revealed that by modifying the clusters preparation procedure either segregated or alloyed Pd-Au clusters can be formed. The composition of the different clusters was also verified by optical surface plasmon resonance (SPR) absorption measurements.

Temperature Programmed Reaction (TPR) measurements have shown that adsorption of acetylene on top of Pd-Au alloy clusters has led to efficient conversion to ethylene. Benzene was also formed at an order of magnitude smaller rate. Pd-Au alloy clusters have demonstrated significantly higher reactivity than the monometallic clusters. Increasing the surface defects density by Ar⁺ ion sputtering enhanced the thermal stability and sintering resistance properties of the Pd-Au clusters.

5:20pm **SS3-TuA11 Reactivity of NO₂ with BaO Nanoclusters Grown on YSZ(111) and CeO₂(111)/YSZ(111) Probed by in situ High-Resolution XPS**, *Z.Q. Yu*, Nanjing Normal University, China, *P. Nachimuthu*, Pacific Northwest National Laboratory, *M. Nandasiri*, *S.V.N.T. Kuchibhatla*, Pacific Northwest National Laboratory, *Y.J. Kim*, Hanbat National University, Korea, *M.H. Engelhard*, *V. Shutthanandan*, *W. Jiang*, *J. Szanyi*, *S. Thevuthasan*, Pacific Northwest National Laboratory
Catalysts for NO_x storage and reduction (NSR) are being developed to reduce the NO_x emission from gasoline based internal combustion engines. BaO is considered to be potential NSR catalysts because of its strong interaction and an effective trapping of NO₂. BaO is more reactive when BaO is present as non-stoichiometric BaO clusters rather than bulk BaO. In order to understand the reactivity, BaO was grown on YSZ(111) and CeO₂(111)/YSZ(111) substrates by molecular beam epitaxy. *In-situ* reflection high-energy electron diffraction, *ex-situ* x-ray diffraction, atomic force microscopy and x-ray photoelectron spectroscopy have confirmed that the BaO grows as nanoclusters on YSZ(111). During and following the growth under UHV conditions, BaO remains in single phase. The reaction of NO₂ with the BaO nanoclusters in different sizes on YSZ(111) and CeO₂(111)/YSZ(111) substrates was investigated using *in situ* high-resolution x-ray photoelectron spectroscopy (XPS). The adsorption of NO₂ on the BaO nanoclusters at room temperature and the formation of Ba(NO₂)₂ species at room temperature and above were probed. In addition the *in situ* XPS data collected from the BaO nanoclusters prior to and following the reaction with NO₂ were utilized to understand the morphology of BaO nanoclusters and the formation of Ba(NO₂)₂ species using Quases-Tougaard V5.1 software. These results are compared with the reported data from NO₂ reaction with BaO film deposited onto an Al₂O₃/NiAl(110) substrate.

* Morton S. Traum Award Finalist

Tribology Focus Topic

Room: B2 - Session TR+SS-TuA

Surface Science for Tribology

Moderator: I. Szlufarska, University of Wisconsin, Madison

2:00pm **TR+SS-TuA1 Effect of the Surrounding Gas Pressure on Charge Separation Caused by Friction between Insulators**, *T. Miura, E. Hosobuchi, S. Ueno, I. Arakawa*, Gakushuin University, Japan

Friction between insulators induces charge separation at the interface. The surface electrification after sliding contact yields electric field in the gap near the contact and results in gas discharge if the friction is carried out in a gas ambience. This gas discharge reduces the charge that was once induced at the frictional interface. It has been believed that the initial charge separation was not affected by a surrounding gas and was determined solely by the frictional materials. We have investigated the charge separation rate before the gas discharge under various gas conditions and found that it linearly decreased with the logarithm of the pressure from 10 Pa to atmospheric pressure for Ne, Ar, and Kr.

The friction experiment was performed by means of pin-on-disk equipment. The pin was made of natural diamond and was gold coated. The disk was quartz or sapphire. The charge accumulated on the gold-coated pin was measured by an electrometer. The diameter of a contact area between the bare diamond tip and the disk was about 10 μm and the sliding velocity was 11 $\mu\text{m/s}$. The charge on the pin increased at a constant rate during sliding and fell to zero when the gas discharge occurred. The charge accumulation and the gas discharge were repeated during sliding friction in a gas ambience. The initial charge density at the interface of the sliding contact was calculated from the accumulation rate, the track width and the sliding velocity.

The charge density was typically the order of 1 mC/m^2 for sliding friction in a vacuum (10 Pa). It was found that the initial charge separation under the atmospheric gas pressure is one order of magnitude smaller than that at 10 Pa. This reduction of the charge separation rate was observed for Ne, Ar, and Kr gas at almost the same efficiency. It is likely that the gas molecules penetrate into the frictional interface and interrupt or relax the charge separation. It should be necessary to investigate the surrounding gas effect on the initial charge separation in detail in order to reveal the origin of triboelectricity.

2:20pm **TR+SS-TuA2 In situ Tribology of Metal-Doped MoS₂: Interfacial Film Mechanics and Friction Behavior**, *K.J. Wahl*, Naval Research Laboratory, *S.D. Dvorak*, University of Maine, *G.Y. Lee, I.L. Singer*, Naval Research Laboratory

Tribological processes that influence friction and wear involve a complex combination of materials science, physics, chemistry, and rheology. Our understanding of these sliding contact phenomena is limited by the fact that all the action takes place in a buried interface. Most often the only evaluation of these interfaces is accomplished through *ex situ* means after separating the contacts. *In situ* approaches to studying friction and wear processes are challenging because most engineering surfaces are metals or ceramics that have no optical transparency at visible wavelengths. For this reason, most of what is known about interfacial processes occurring during sliding has been learned through optical probes of sliding interfaces.

We have used an *in situ* tribometer to perform reciprocating sliding tests of Pb-Mo-S and Ti-Mo-S solid lubricant coatings. Experiments were performed in dry and ambient air. The interfacial films formed during sliding were monitored with *in situ* Raman spectroscopy and optical microscopy through transparent counterfaces. The dominant velocity accommodation mode in both dry and humid conditions was interfacial sliding between the surface of the wear track and the outer surface of the transfer film on the counterbody. Humid air sliding resulted in a second velocity accommodation mode involving shear and/or extrusion of the transfer film. We will demonstrate and discuss how the interface properties – shear strength and transfer film mechanical properties – affect friction behavior of these solid lubricant coatings.

2:40pm **TR+SS-TuA3 Nanosecond X-Ray Pulses From Peeling Tape in Vacuum**, *S. Putterman, J.V. Escobar, C.B. Camara, J. Hird*, University of California, Los Angeles

INVITED

That the surface between two interacting bodies can be a source of visible light –triboluminescence– has been known for centuries. Observation of the emission of nanosecond long 100.mW pulses of X-Ray photons from peeling tape indicates that tribological processes reach energy densities which are much greater than the few eV per molecule needed to generate visible photons. Analysis of the x-ray pulses indicates that they originate

from micron scale regions near the vertex of peeling tape. Based upon this insight we are building a mechanically operated sub-millimeter x-ray source that can be used for medical imaging. The organized processes which transduce diffuse mechanical energy into x-ray pulses are not understood.

4:00pm **TR+SS-TuA7 Nanotribology at Cryogenic Temperatures**, *S.S. Perry, X. Zhao, S.R. Phillpot, G. Sawyer, S.B. Sinnott*, University of Florida

The temperature dependence of the kinetic friction between a silicon nitride probe tip and a number of crystalline surfaces has been evaluated through atomic force microscopy measurements performed under an ultrahigh vacuum environment over the temperature range 140-750 K. Surfaces interrogated include highly oriented pyrolytic graphite, molybdenum disulfide, and lead sulfide. A relatively weak dependence on temperature is observed in the friction measured between 300 K and 750 K. As temperature decreases below ambient temperatures, a sharp increase in friction is observed for all surfaces, however with variations in the temperature threshold. Collectively, these results obtained from fundamental interfaces are consistent with an activated mechanism of energy dissipation during sliding. An Arrhenius analysis of the temperature dependent friction over this range yields different effective activation energies, ranging from 0.1-0.4 eV for the thermally activated stick-slip motion of the probe tip on this surface. As temperature is reduced further, a distinct transition to a largely athermal behavior is detected and is shown to result from the onset of interfacial wear, entailing an alternative energy dissipation pathway.

4:20pm **TR+SS-TuA8 Molecular Dynamics Simulations of Nanoindentation of Si/SiO₂ Systems using the Charge Optimized Many-Body (COMB) Potential**, *T.R. Shan, B. Devine, S.R. Phillpot, S.B. Sinnott*, University of Florida

Oxides and carbides, such as SiO₂, Al₂O₃, HfO₂ and SiC, are widely used together with Si in many high-performance electronic devices, including metal-oxide-semiconductor (MOS) devices/junctions and gate stacks. The lack of precise control over mechanical properties can lead to the degradation of these materials. It is therefore critical to understand the nanometer-scale mechanical properties of materials or complex systems being considered for use in electronic devices. Since nanoindentation has been established as a primary tool for investigating the mechanical behavior of small volumes of materials, classical molecular dynamics simulation is used to examine the nanoindentation of Si/SiO₂ interfacial systems. Because these systems consist of heterogeneous interface with significant changes in bonding as one crosses from one side of the interface to the other, the empirical charge optimized many-body (COMB) potential is used to model the structural evolution, mechanical response and charge transfer of Si/SiO₂ interfacial systems under the influence of a nanometer-scale indenter. The COMB potential allows for dynamic charge transfer between atoms and across interfaces, and does a good job in describing covalent and ionic bonding in these materials. Aspects of the Si/SiO₂ interface during nanoindentation, including dislocation formation and the mechanisms by which fracture occurs, will also be addressed. We gratefully acknowledge the support of the National Science Foundation through grant DMR-0426870.

4:40pm **TR+SS-TuA9 Influence of Molecular Structure and Alignment on Nanometer-Scale Tribology**, *P. Barry, P. Chiu, S.R. Phillpot, S.B. Sinnott*, University of Florida

We report on the effect of small, fluorocarbon molecules on self-mated, aligned polytetrafluoroethylene (PTFE)-PTFE tribology using atomistic molecular dynamics simulations. Three fluorocarbon molecular classes were considered: C₂F₆, C₄F₁₀ and C₈F₁₈ with the amount of lubricant between the classes kept constant. Further, the effects of a relatively thin lubricating layer and a relatively thick lubricating layer were compared. The simulations predicted that the systems with thicker lubricating layers exhibited a friction coefficient that was significantly lower than those a thinner lubricating layer. Correspondingly, substantially more molecular wear of the PTFE surfaces were predicted for the latter systems. Interestingly, unlubricated PTFE-PTFE self-mated systems demonstrated low friction coefficients and molecular wear when the chains were slid in a direction parallel to the chain alignment, and unlubricated, aligned polyethylene (PE)-PE systems exhibited comparable or lower friction coefficients. The simulations further predicted that unlubricated, aligned PE-PTFE systems had friction coefficient values in between those of the PE-PE systems and PTFE-PTFE systems in which the chains slid in directions that were perpendicular to the alignment of the chains. Surprisingly, the highest friction coefficients in the PE-PTFE system occurred when the chains were slid in a direction parallel to the direction in which the chains were aligned. This result was attributed to the incommensurate nature of the sliding interface between the two different polymers. This work was carried out under the support of an AFOSR MURI.

5:00pm **TR+SS-TuA10 On the Mechanical Properties of Tungsten Disulfide Nanotubes**, *I. Kaplan-Ashiri, S.R. Cohen, K. Gartsman, Weizmann Institute of Science, Israel, G. Seifert, Technische Universität, Germany, H.D. Wagner, R. Tenne, Weizmann Institute of Science, Israel*

WS₂ forms multiwalled nanotubes which seem to be almost defect free and their structure can be precisely defined. Hence they can serve as good candidates for the study of nanomechanics.

Various mechanical tests were applied on individual WS₂ nanotubes to reveal their mechanical properties and behavior. First, nanotubes were axially compressed in atomic force microscope, and their Young's modulus was observed according to Euler's buckling point. An average value of 170GPa was obtained. A similar test which was conducted in the scanning electron microscope resulted in large elastic deformation of the nanotube. Here the Young's modulus was obtained from the post buckling equations, and found to be 150GPa. In a third experiment, the nanotubes were axially strained until fracture occurred. The Young's modulus was then observed according to Hooke's law and found to be 152GPa. These moduli values are in good agreement between themselves and also with density functional tight-binding (DFTB) calculations and the bulk material (150GPa).

Tensile strengths and strain values as high as 16GPa and 14% were observed as well. These values reveal that WS₂ nanotubes reached their theoretical strength, hence they are suspected to be defect free. The high strain value is unique to the tubular nanophase of WS₂ and is also in good agreement with molecular dynamics simulation of MoS₂ nanotubes. The nanotubes were deformed elastically until failure, in "sword in a sheath" mechanism and probably fractured in a brittle mode.

Clamped nanotubes were bent and the shear (sliding) modulus was obtained according to Timoshenko's bending equation and found to be 2GPa. This value is in good agreement with DFTB calculations (4GPa) for sliding of two adjacent layers of MoS₂.

Furthermore, a unique nonlinear elastic deformation was observed both in post buckling and in bending tests. This mode of deformation is associated with the tubular structure.

5:20pm **TR+SS-TuA11 Nanotribological Characterization of Various Skin Cream Ingredients using Atomic Force Microscopy**, *W. Tang, B. Bhushan, The Ohio State University, S. Ge, China University of Mining and Technology*

Skin cream is used to improve skin health and create a smooth, soft, pliable, and moist perception by altering the surface friction, adhesion, elastic modulus, and surface potential of the skin surface. As the industry continually searches for better cream formulations, it becomes increasingly necessary to study how different cream ingredients interact with skin surface on the nanoscale. In this paper, vaseline, glycerin, and lanolin oil, which are the widely used ingredients in moisture cream, as well as the common moisture cream, advanced moisture cream, and oil-free moisture cream, were studied using an atomic force microscope (AFM). The binding interaction between skin cream and skin surface is one of the important factors in determining cream thickness and consequently the proper performance of skin cream. Film thickness, adhesive force and effective Young's modulus of various cream treated skin was measured using the force calibration plot technique with the AFM. Skin goes through various daily activities with time and the durability properties are closely tied to product performance. The durability of various skin creams were studied by repeated cycling tests. The health and feel of skin are significantly affected by its surface charging and the surface potential of virgin skin, and various cream treated skin was measured to determine the effects of various skin cream using the Kelvin probe method with the AFM. Relevant mechanisms are discussed.

5:40pm **TR+SS-TuA12 An Imaging TOF-SIMS Study of the Tribochemical Interactions in Diamondlike Carbon Films**, *A. Erdemir, O. Eryilmaz, Argonne National Laboratory*

Diamondlike carbon (DLC) films combine many attractive properties which make them good prospect for a wide range of engineering applications. Depending on the sources of carbon (i.e., hydrocarbon gases or solid carbon or graphite targets) and the type of deposition method, some of the DLC films may contain large amounts of hydrogen in their structures and they are relatively soft. Those that are produced from solid carbon and/or graphite targets by arc-PVD and pulsed laser deposition are nearly hydrogen free but very hard. However, regardless of their chemical and/or structural nature, all DLC films tend to be very sensitive toward the chemical composition of the test environments when tested for their friction and wear properties. In this study, we concentrate our attention on the friction and wear behaviors of both the hydrogenated and hydrogen-free DLC films in the presence of inert and reactive gaseous species like, argon, oxygen, hydrogen, and deuterium in test chambers. Using time-of-flight secondary electron mass spectrometry (TOF-SIMS), we explore the extent of tribochemical interactions that occurred during sliding tests. These

studies have confirmed that the friction and wear behaviors of DLC films are indeed very closely controlled by the type and extent of tribochemical events that are triggered by the gaseous species in the surrounding atmosphere. In particular, hydrogen and deuterium in test environments seems to interact with the sliding surfaces of these films and thus have the greatest effect on friction and wear. Inert gases were detrimental for the friction and wear behaviors of hydrogen-free DLC, but beneficial to that of the highly hydrogenated DLC films. Based on the results from TOF-SIMS studies, we provide a mechanistic explanation for the tribochemistry of sliding surfaces and correlate these findings with the friction and wear behaviors of DLC films.

Tuesday Afternoon Poster Sessions

Surface Science

Room: Hall 3 - Session SS-TuP

Surface Science Poster Session I and Mort Traum Finalists

SS-TuP1 MORTON S. TRAUM AWARD FINALIST: Morphology and Chemical Reactivity of Bi-Metallic Au-Pd Clusters, E. Gross*, M. Asscher, The Hebrew University of Jerusalem, Israel

Bi-metallic clusters have unique catalytic properties, since one metal can modify the electronic and thus the catalytic properties of the other metal. Here we describe a unique preparation method of bimetallic Pd-Au nano-clusters. The growth mode is based on initial evaporation of metal atoms on top of amorphous solid water adsorbed on SiO₂/Si(100) substrate at 100K under ultra high vacuum (UHV) conditions. The ice buffer layer separates the small metallic seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth of nano-clusters in a Buffer Layer Assisted Growth (BLAG) mechanism.

Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) measurements revealed that by modifying the clusters preparation procedure either segregated or alloyed Pd-Au clusters can be formed. The composition of the different clusters was also verified by optical surface plasmon resonance (SPR) absorption measurements.

Temperature Programmed Reaction (TPR) measurements have shown that adsorption of acetylene on top of Pd-Au alloy clusters has led to efficient conversion to ethylene. Benzene was also formed at an order of magnitude smaller rate. Pd-Au alloy clusters have demonstrated significantly higher reactivity than the monometallic clusters. Increasing the surface defects density by Ar⁺ ion sputtering enhanced the thermal stability and sintering resistance properties of the Pd-Au clusters.

SS-TuP2 MORTON S. TRAUM AWARD FINALIST: Direct Observation of Hydrogen-Bond Exchange within a Single Water Dimer, T. Kumagai*, M. Kaizu, H. Okuyama, Kyoto University, Japan, S. Hattai, T. Aruga, Kyoto University, JST-CREST, Japan, I. Hamada, Y. Morikawa, Osaka University, Japan

The nature of the hydrogen bond is related to many physical, chemical and biological processes. The structure and dynamics of water dimers, which consist of hydrogen-bond donor and acceptor molecules, have been subjects of extensive research as a prototype of much more complex hydrogen-bonding systems. The water molecules in a free water dimer rearrange the hydrogen bond through quantum tunneling among equivalent structures [1]. Recently, we reported the visualization in real space of hydrogen-bond exchange process governed by quantum tunneling within a single water dimer adsorbed on a metal surface with a low-temperature scanning tunneling microscope (STM) [2].

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM operating at 6 K. The Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H₂O or D₂O gases via a tube doser below 20 K. We conducted the experiments at very low coverages, where water molecules exist mainly as isolated monomers and dimers on the surface.

A water dimer is characterized by its bi-stable fluctuating image due to the interchange motion of the hydrogen-bond donor and acceptor molecules. The STM image of the dimer shows dramatic change upon substitution with heavy water. The interchange motion of (D₂O)₂ is much slower than that of (H₂O)₂. The interchange rate was determined to be $(6.0 \pm 0.6) \times 10^{-1}$ s⁻¹ for (H₂O)₂ and 1.0 ± 0.1 s⁻¹ for (D₂O)₂ by monitoring the interchange events in real time. The large isotope effect (~60) suggests that the rate-limiting process involves quantum tunneling. In addition, DTF calculation revealed that the barrier of the interchange on Cu(110) is 0.24 eV. This cannot be overcome via mere thermal process at 6 K, which corroborates that the interchange proceeds through tunneling.

Furthermore, the interchange rate is enhanced upon excitation of the intermolecular mode that correlates with the reaction coordinate. While the interchange motion is intrinsic at low bias voltage, as indicated by negligible tip effect, it becomes tip assisted at voltages above 40 mV. The threshold voltage is determined to be 45 ± 1 (41 ± 1) mV for H₂O (D₂O) dimers. The barrier for the interchange (0.24 eV), however, much larger than the energy transferred from a tunneling electron (45 mV).

Consequently, we propose that the interchange tunneling is assisted by vibrational assisted tunneling process.

[1] R. S. Fellers, C. Leforestier, L. B. Braly, M. G. Brown, and R. J. Saykally, *Science* 284, 945 (1999).

[2] T. Kumagai *et al. Phys. Rev. Lett.* 100, 166101 (2008).

SS-TuP3 MORTON S. TRAUM AWARD FINALIST: A Surface-Chemical Perspective on the Success (and Failure) of Metalorganic Compounds as Precursors for Thin Film Deposition, J.C.F. Rodriguez-Reyes*, A.V. Teplyakov, University of Delaware

Fundamental studies focused on understanding the key surface processes that introduce contaminants into a growing film are essential for achieving a contaminant-free thin film deposition. In the case of the metal alkylamide precursor Ti[N(CH₃)₂]₄, we have obtained experimental evidence of two chemical reactions on a Si(100) surface that explain the uncontrolled incorporation of carbon during deposition, namely a surface attachment through a ligand and a feasible C-H bond scission on the surface. For both reactions, the nitrogen p-orbital in the alkylamide precursor plays a significant role, not only favoring the interaction of a N atom with electron-deficient surface sites, but also weakening anti-periplanar C-H bonds. The realization of the important role that the heteroatom in the ligand plays during surface reactions prompted us to start a comprehensive computational investigation of N-containing and O-containing metalorganic precursors, such as amidinates, guanidinates, alkoxides and acetonates. In addition, we consider metal alkyls and cyclopentadienyl precursors. An effective comparison of the surface reactivity of these compounds and their ability to adsorb and decompose on a surface is achieved by simulating the reactions on a silicon surface cluster model using the same methods. Our results corroborate the model established for the alkylamide precursors, where metalorganic precursors adsorb preferentially through the formation of a N- or O- dative bond to the surface. However, further decomposition mechanisms are less favorable for certain types of precursors, such as amidinates and guanidinates, where the p-orbital of the N atoms is delocalized and therefore does not favor the scission of nearby C-H bonds. Oppositely, alkylamides, alkoxides and acetonates are found to readily decompose on the surface. When heteroatoms are absent (e.g. in the case of cyclopentadienyls) adsorption is a significantly less favorable process and decomposition pathways leading to carbon incorporation are less feasible than for other compounds. This investigation is intended to set a ground work for future investigations devoted to understanding and controlling contamination mechanisms during film deposition.

SS-TuP4 MORTON S. TRAUM AWARD FINALIST: Nanoparticle Growth from Copper Metal-Organic Precursors on H-terminated Silicon Surfaces, K.A. Perrine*, A.V. Teplyakov, University of Delaware

Scaling down of the features needed for microelectronic industry has been redefined with the advances in atomic layer deposition (ALD) methods. At the same time, chemical vapor deposition (CVD) of copper has been used in interconnect devices in the electronics industry for several decades. For a controlled copper deposition, it is desirable to combine the clean ligand removal from the precursor molecules (such as, Cu^I (hexafluoroacetylacetonato) vinyltrimethylsilane or Cu(hfac)VTMS) with the control of the ALD process.

In this work, copper nanoparticles were grown by CVD on hydrogen-terminated silicon surfaces to minimize interfacial contamination and effectively remove the hfac and VTMS ligands for clean Cu deposition. During the deposition process, the amount of copper deposited at room temperature is limited by the amount of hydrogen available for ligand removal. Both H-terminated Si(111) and Si(100) surfaces exhibit the growth of nanoparticles, as observed by AFM, and the amount of copper deposited depends on the amount of surface hydrogen present, showing similarity to ALD growth mechanism. Both AFM and SEM confirm copper nucleation. In addition, the growth kinetics of Cu(hfac)VTMS is compared for monohydrogen-terminated Si(100) and hydrogen-terminated Si(100)-3x1 using *in situ* MIR-FTIR. The growth on OH- and NH- terminated surfaces will be compared to that on H-terminated surfaces. *In situ* FTIR spectroscopic studies indicate surface reaction by analysis of the Si-H region and are compared to *in situ* and *ex situ* XPS studies to confirm metallic copper deposition. Silicon surfaces, Si(111) and Si(100), yield different results and indicate that copper growth starts at defect sites. These results set a foundation for growth of clean copper on reducing solid substrates.

* Morton S. Traum Award Finalist

SS-TuP5 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene, Q.H. Wang*, M.C. Hersam, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al₂O₃ on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,¹ and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.² In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.³ We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

¹ X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).

² P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).

³ Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

SS-TuP6 MORTON S. TRAUM AWARD FINALIST: Size-Dependent Catalytic Properties of Pt Nanoparticles Synthesized by Reverse Micelle Encapsulation: Oxidation, Reduction, and Reactivity, J. Croy*, L.K. Ono, S. Mostafa, H. Heinrich, B. Roldan Cuenya, University of Central Florida

The oxidation of Pt and the reactivity of Pt oxides are of fundamental importance in catalysis, and although much research has been conducted on the interaction of oxygen with Pt surfaces, most of the work is confined to UHV with bulk materials such as Pt(111). In this work we will explore the size-dependent oxidation and reduction properties of Pt nanoparticles (NPs) synthesized by reverse micelle encapsulation. We use in-situ O₂-plasma treatments in conjunction with e-beam heating and X-ray photoelectron spectroscopy (XPS) to monitor the temperature-dependent reduction of Pt^{δ+} species in NPs with distinct size distributions. In addition temperature programmed desorption (TPD) was conducted to monitor the oxygen phases developed on our NP samples. These results are compared with the same experiments conducted on a Pt(111) crystal. In parallel to UHV studies, the activity of pre-oxidized Pt NPs, supported on nanocrystalline ZrO₂, was tested for methanol (MeOH) decomposition and oxidation reactions at atmospheric pressure using a packed-bed reactor coupled to a quadrupole mass spectrometer (QMS). Transmission electron microscopy (TEM) was conducted for morphological information and XPS was used to characterize samples both before and after interaction with MeOH.

SS-TuP7 A Novel Spectrometer for Wide Angle and High Pressure Photoemission, A. Thissen, S. Mähl, T. Kampen, O. Schaff, SPECS GmbH, Germany

New scientific opportunities in key research fields like catalysis, research on liquid and aqueous samples, and living matter demand a combination of in-situ x-ray photoemission experiments (XPS) with high-pressure environments of up to 10 mbar.

To address these exciting new challenges we have developed a novel photoemission spectrometer that enables angle resolved photoelectron spectroscopy (XPS) at pressures up to 10 mbar with an angular acceptance of +/- 22°. This new set-up not only dramatically increases the spectrometer transmission but also allows non-destructive depth profiling exploiting the angular dependence of the XPS signal.

* Morton S. Traum Award Finalist

The instrument consists of a differentially pumped PHOIBOS 150 hemispherical analyzer with a pre-lens. This newly developed pre-lens increases the acceptance angle of the PHOIBOS analyzer by a factor of 5. At the same time it allows extremely efficient differential pumping of the gas atmosphere above the sample.

SS-TuP8 In Situ High Pressure X-ray Photoelectron Spectroscopy Studies of the Adsorption of CO and O₂ on Au Nanoparticles Grown on TiO₂(110) Surfaces, P. Jiang, S. Porsgaard, F. Borondics, M. Kober, Z. Liu, M. Salmeron, H. Bluhm, Lawrence Berkeley National Laboratory

Gold nanoparticles supported on TiO₂ surfaces are effective catalysts for CO oxidation. Despite numerous studies on this system, the fundamental mechanism is still controversial, partly due to the challenging pressure gap. Using our special in situ high pressure X-ray photoelectron spectroscopy (HP-XPS), we systematically investigated the adsorption of CO and O₂ on Au nanoparticles grown on TiO₂(110) surfaces with different stoichiometries under real reaction conditions. We found that the synergism between Au and TiO₂ surfaces plays the key role for the whole reaction process.

SS-TuP10 DFT Study of Oxygen Vacancy Formation in a Diesel Oxidation Catalyst: Pt/CeO₂(111), T.Q. Nguyen, M.C.S. Escanho, S. Kunikata, H. Nakanishi, H. Kasai, Osaka University, Japan, H. Maekawa, K. Osumi, Y. Tashiro, Isuzu Advanced Engineering Center, Ltd., Japan

Air pollution from automobile exhaust is one of the major environmental problems in modern civilization. In order to reduce the amount of noxious pollutants, the diesel oxidation catalyst (DOC) systems are widely used. In the DOC system, CO and Hydrocarbon (HC) are oxidized to harmless chemical substances such as H₂O, CO₂, and NO is converted to NO₂.¹⁻⁴ DOCs have a honeycomb-like, monolithic structure. The monolith support is made either from metallic (stainless steel) or ceramic material and coated with a so-called "washcoat". The washcoat consists of high porous oxides, such as γ -Al₂O₃ (alumina), and precious metals, such as Pt, Pd, and Rh plus more additives (e.g., CeO₂ and ZrO₂) to increase the catalytic activity or to stabilize the structure of the catalyst. In DOCs, Cerium is present in high quantities in the form of CeO₂. Cerium renders multiple functions, the most vital of which is to store and to release oxygen under fuel-lean and fuel-rich conditions. This is so-called the oxygen storage capacity (OSC), which allows the catalyst to operate over wider air to fuel ratio.⁵

In this work, we investigate the adsorption of Pt atom on unreduced and reduced CeO₂(111) surface by using first-principles method. With the aim of having a better understanding of the catalytic properties of Pt/CeO₂ for further development and improvement of DOCs, we concentrated on the details of Pt adsorption on CeO₂, the formation of oxygen vacancies at Pt/CeO₂ surfaces and how it affects the geometric and electronic structures as well as chemical properties of surface. We found that, some metal induced gap states appeared under the adsorption of Pt, which is due to the strong interaction between Pt 5d and O 2p. This is the factor that makes the Pt/CeO₂ system more active than the clean CeO₂ surface. In addition, the adsorption of Pt accelerates the formation of surface vacancies and enhances the OSC. A more detailed discussion of these results will be conducted in the meeting.

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- ⁵ H. C. Yao, Y. F. Yu. Yao, *J. Catal.* **86** (1984) 254

SS-TuP11 Surface Electronic Structures and Chemical States of O₂ on Pt₃M [111], (M = Fe,Co,Ni), Y.-S. Kim, Lawrence Berkeley National Laboratory and Hanyang University, Korea, **B.S. Mun,** Hanyang University, Korea and Lawrence Berkeley National Laboratory, **V. Stamenkovic, N. Markovic,** Argonne National Laboratory, **A. Bostwick, E. Rotenberg, P.N. Ross,** Lawrence Berkeley National Laboratory

With x-ray photoemission spectroscopy (XPS), surface electronic structures and chemical states of O₂ on Pt₃M [111] single crystals are investigated at various surface temperature, T = 30~150K. At T=30K, both physisorbed and chemisorbed oxygen molecules are present on the surfaces. As the surface temperature is increased to 150K, molecular oxygen on the surface undergoes a phase transition from weakly bounded physisorbed states to chemisorbed states, i.e. an atomic oxygen states. From the measurements of Fermi surface with angle-resolved XPS, Pt [111] surface shows a clear signature of charge transfer along M direction upon the adsorption of oxygen molecules. However, all other Pt₃M surfaces exhibit little changes

near Fermi surface at various temperatures. The correlation between the electrochemical reactivity and surface electronic structures on Pt₃M will be presented.

SS-TuP13 Improvement of Metal Oxide Catalyst Reactivity by Modification of Surface Fermi Level. *M.C. Kratzer*, University of Illinois at Urbana-Champaign, *F. Nasim, A.S. Bhatti*, Comsats Institute of Information Technology, Pakistan, *E.G. Seebauer*, University of Illinois at Urbana-Champaign

There is good reason to believe that the properties of semiconducting metal oxide catalysts can be improved when designed according to the principles of microelectronic devices. Since metal oxide semiconductors support space charge, it is possible for surface electronic properties to couple to bulk electronic properties. Consequently, electronic "band engineering" can be employed to optimize surface reactivity and affect either thermal catalysis or photocatalysis. For instance, hydroxyl group acidity on the TiO₂ surface can be tuned via the electron richness of the semiconductor, which can be manipulated via controlled doping. Alternatively, the direction and magnitude of the near-surface electric field within the space charge region can be adjusted by bulk doping which, in turn, affects the flow of photogenerated charge carriers toward the surface in photocatalysis. The present work describes the applicability of photoreflectance (PR), a type of modulation spectroscopy, to understanding semiconductor surface-bulk coupling in the context of catalysis using TiO₂ as an example metal oxide. The approach involves the synthesis of a thin film of the semiconductor on a silicon substrate by chemical vapor deposition or atomic layer deposition. N- and p-type dopants are introduced into TiO₂ during deposition to produce samples of varying doping levels. The physical and chemical properties of the thin films are characterized using ellipsometry, x-ray diffraction, and x-ray photoelectron spectroscopy. Detailed electrical characterization employing a Schottky diode test structure is undertaken to obtain a precise estimate of carrier concentration. PR is then utilized to better understand the effect of film thickness and uniformity, crystal structure, and doping on the position of the surface Fermi level. The results shed light on the properties of the TiO₂ surface as it relates to thermal catalysis and photocatalysis, and enable unprecedented precision in the tailoring of metal oxide catalysts to ensure optimal surface reactivity.

SS-TuP18 Transition of the Molecule Orientation during Adsorption of Terephthalic Acid on Rutile TiO₂. *A. Nefedov*, Ruhr University of Bochum, Germany, *P. Rahe, M. Nimmrich*, University of Osnabruck, Germany, *M. Naboka*, Ruhr University of Bochum, Germany, *A. Kuehnle*, University of Osnabruck, Germany, *Ch. Woell*, University of Bochum, Germany

Chemically functionalized surfaces play an important role in many nanotechnological applications. However, only few attempts have been made so far to create a chemically functionalized metal oxide surface by adsorption of organic molecules, even though metal oxide surfaces provide anisotropy and specific adsorption sites that lead to well-ordered monolayers. Terephthalic acid (TPA) is a versatile molecular linker and has, consequently, received considerable attention with regard to the assembly of three-dimensional self-assembling porous frameworks stabilized by metal-carboxylate bonds, as well as in two-dimensional supramolecular architectures at surfaces. In particular, TPA/TiO₂ is a promising system to create an overlayer of upright oriented molecules exposing an organic surface terminated by carboxyl groups.

The coverage-dependent adsorption of terephthalic acid on rutile TiO₂ was investigated by means of non-contact atom force microscopy (NC-AFM) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy [1, 2] under ultra-high vacuum conditions at room temperature. Experiments were performed in two separate systems, one for performing the NC-AFM measurements and the second UHV system using synchrotron radiation for the NEXAFS experiments, which were carried out at the HE-SGM beamline of BESSY II.

Individual molecules are observed to adsorb in a flat-lying geometry at low coverages up to ~0.3 monolayer (ML). The molecules are immobile at room temperature, implying a diffusion barrier of larger than 0.8 eV. This rather high value might be explained by an anchoring to surface defect sites. A transition from flat-lying to upright-oriented molecules is revealed by NEXAFS when saturation coverage is achieved. High resolution NC-AFM images reveal two different structures at coverages between ~0.8 ML and 1 ML: (i) a well-ordered (2×1) structure and (ii) a mixed structure of molecular rows oriented along the [001] crystallographic direction. The latter structure might originate from a pairwise interaction of two neighboring molecules through the top carboxyl groups. Further increase of the exposure results in a saturation of the corresponding signal in the NEXAFS spectra revealing that the growth of TPA on TiO₂ at room temperature is self-limiting.

1. S. Reiss, H. Krumm, A. Niklewski, V. Staemmler, Ch. Wöll, J. Chem. Phys. 116, 7704, (2002).

2. D. Käfer, L. Ruppel, G. Witte, Ch. Wöll; Phys. Rev. Lett., 95, 166602 (2005).

SS-TuP19 Effect of Rapid Thermal Annealing on the Electrical and Optical Properties of Reactively Sputtered Ag₂O Thin Films. *C.C. Tseng*, National Chung Hsing University, Taiwan, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, *W. Wu*, National Chung Hsing University, Taiwan

Silver oxide films were deposited on glass substrates by magnetron sputtering of a silver target in various Ar-O₂ reactive mixtures with deposited temperature. After deposition, some of these films were annealed using a rapid thermal annealing (RTA) system, with the variation of temperature. A UV-VIS-NIR photometer and a Hall measurement system were used to characterize the optical and electrical properties of these films. The films show a systematic change from Ag₂O(hexagonal) phase to Ag+Ag₂O(cubic) phases at various annealing temperatures. When the annealing temperature is higher than 300°C, the Ag₂O(hexagonal) phase transformed to Ag+Ag₂O(cubic) composite phases. Accordingly, the band gap of these films will change, along with the optical and electrical properties.

Keywords: silver oxide, UV-VIS, rapid thermal annealing, optical property, electrical property.

Wednesday Morning, November 11, 2009

Surface Science

Room: M - Session SS1-WeM

Water/Surface Interactions & Environmental Chemistry I

Moderator: D.R. Strongin, Temple University

8:00am **SS1-WeM1 Scanning Probe Microscopy of Interfacial Water Confined Between Silica Surfaces**, *B.I. Kim, J.R. Bonander, E.J. Kim, T. Tran*, Boise State University

Scanning probe microscope (SPM) techniques are employed to study the structure and mechanical properties of water confined between two silica surfaces. Water molecules adjacent to other materials, such as in the vicinity of biological cell membranes, rearrange to form "interfacial water." The interfacial water behaves differently from bulk water to a substantial degree in its structure and mechanical properties. Probing the structure of interfacial water and its mechanical properties is crucial from understanding of the biomolecular functions to the micro-machine development. Even with such importance, however, the interfacial water is difficult to observe with ordinary analytic techniques because of its delicate nature near the surface. The SPM's excellent distance and force control capability allows for investigating the interfacial water near the sample surface. A cantilever based optical interfacial force microscope (COIFM), a newly developed SPM technique at Boise State University, was used to probe the ordered structure of the interfacial water in the direction perpendicular to the surface. A Non-Contact (NC) AFM was used to image the arrangement of the interfacial water in the direction parallel to the surface. The COIFM and NC-AFM measurements were performed on silica surfaces, the most abundant substance on the earth's crust, for various relative humidity. The COIFM data show periodic features as the tip approaches the surface, showing single water-layer ordering effect of the interfacial water. In each layered region, the force decreases nonlinearly as the gap decreases. The NC-AFM images show that some water bundles lay down and some stand up, supporting the COIFM data. The humidity dependent data shows how the structure of water evolves as the thickness of the water film changes from droplets to monolayers to multilayers on the silica surface. The origin of the observed structure of the interfacial water is discussed with a simple two-dimensional self-assembly theory.

8:20am **SS1-WeM2 Theory of Tip-Sample Interaction Force for AFM in Water**, *M. Tsukada*, Tohoku University, Japan

Noncontact AFM(ncAFM) in aqueous condition is an important method for imaging soft biological nano materials as protein. We are attempting theoretical simulation for the atomic force microscopy(AFM) in water[1,2]. So far we found various remarkable features of tip-surface interaction force mediated by water molecules[2]. They are obtained either by the molecular dynamics (MD) calculation or by the 3D-RISM (Reference Interacting Site Model) calculation.

As an example of the numerical simulation by MD method, AFM images and 3D force map of mica surface in water were calculated and compared with the experiments by Yamada's Group. The oscillatory layer structures of water exist around the interface tracing the nano-scale shapes of the sample. The phase and the amplitude of the force oscillation felt by the tip are remarkably changed depending on the lateral tip position, resulting a complicated network structure of the 3D force map. The number of the water layers in the narrow gap between the tip and sample decreased abruptly and finally disappears when the tip approaches to the surface.

The 3D-RISM method was applied to clarify the local charge separation effect on the interaction force in water. The distribution of water molecules around the atomically charged portion on the substrate is significantly disturbed, and this effect is observed in the 3D-force map from much far region as compared with that in vacuum. We discuss how drastically different the water mediated tip-sample force compared with that in vacuum, and how they influence on the images.

[1]M. Tsukada, N. Watanabe, *Jpn.J.Appl.Phys.*, vol.48 No.3 2009

[2] Tsukada, Tagami, *Phys. Rev. B* submitted.

8:40am **SS1-WeM3 Isolated Single Water Molecules on Ultrathin MgO Film Studied by Scanning Tunneling Microscope**, *H.-J. Shin, J. Jung, K. Motobayashi*, RIKEN and University of Tokyo, Japan, *Y. Kim*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

The interaction of water molecules with solid surfaces has been a subject of considerable interests, due to its importance in the fields from atmospheric and environmental phenomena to biology, catalysis and electrochemistry [1-2]. Among various kinds of surfaces, a lot of theoretical and experimental studies have been performed regarding water on MgO(100), however, to date, there has been no direct observation of water molecules on MgO by scanning tunneling microscope (STM) as compared with those on metal surface. Here, we will present the direct observation and manipulation of single water molecules on ultrathin MgO(100) films using low-temperature scanning tunneling microscope (LT-STM). Our results rationalize the previous theoretical predictions of isolated water molecules on MgO including the optimum adsorption sites and non-dissociative adsorption of water. Moreover, we were able to dissociate a water molecule by exciting the vibrational mode of water, which is unattainable on metal surfaces. The enhanced residual time of tunneling electrons in molecules on the insulating film is responsible for this unique pathway toward dissociation of water.

[1] P. A. Thiel and T. E. Madey *Surf. Sci. Rep.* **7**, 211 (1987).

[2] M. A. Henderson, *Surf. Sci. Rep.* **46**, 5 (2002).

9:00am **SS1-WeM4 In Situ XPS Study of H₂O and CO₂ Adsorption on MgO(100) Films under Ambient Conditions**, *J. Newberg, D. Starr, E. Mysak*, Lawrence Berkeley National Lab, *S. Yamamoto, S. Kaya*, Stanford Synchrotron Radiation Lab, *T. Kendelewicz*, Stanford University, *S. Porsgaard, M. Salmeron*, Lawrence Berkeley National Lab, *G. Brown, Jr.*, Stanford University, *A. Nilsson*, Stanford Synchrotron Radiation Lab, *H. Bluhm*, Lawrence Berkeley National Lab

Under ambient relative humidity (RH) conditions thin film water coats metals, insulators, semiconductors and ice surfaces [1]. The water-oxide interface plays an important role in chemical, biological and industrial systems [2]. Water on MgO(100) is one of the most widely studied systems, both theoretically and experimentally, due to the simple rock salt cubic structure of MgO. Carbon dioxide is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for carbon dioxide sequestration [3]. Here we present results from the investigation of the interaction of water and carbon dioxide with MgO(100)/Ag(100) films using the ambient pressure photoemission spectroscopy (APPEs) setup at beamline 11.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory [4]. With APPEs we can quantitatively probe on a molecular level the chemical changes of the MgO(100) surface using XPS and NEXAFS while in equilibrium with water and/or carbon dioxide gases. Using 0.5 Torr isobars, we have characterized the uptake of water on MgO surfaces up to 20% RH. At roughly 0.1% RH, the MgO surface is fully hydroxylated with a ML of OH and sub-ML molecular water. At 20% RH there is roughly 1 ML of molecular water interacting with a fully hydroxylated MgO surface. Preliminary results for carbon dioxide reactivity with MgO to form carbonate showed dependency on whether the MgO surface was dry (oxide terminated) or wet (hydroxyl/water terminated). Thus, the presence of thin film water influences carbon sequestration. Ongoing studies are addressing the influences of changing RH on MgO carbonation.

References

[1] G.E Ewing 2006 *Chem Rev.* **106** 1511.

[2] G.E. Brown et al. 1999 *Chem. Rev.* **99** 77.

[3] T. Koljonen et al. 2004 *Energy* **29** 1521.

[4] H. Bluhm et al. 2007 *MRS Bulletin* **34** 1022.

9:20am **SS1-WeM5 Oxide and Carbonate Surfaces in Dynamic Equilibrium with Water Vapor**, *V. Grassian*, University of Iowa
INVITED

Adsorbed water plays an important role in a wide range of surface phenomena. In this talk, the focus is on water interactions with oxide and carbonate surfaces in dynamic equilibrium with water vapor under ambient conditions of temperature and relative humidity. The coverage and nature of the adsorbed water layer as a function of relative humidity are investigated. Both experiment and theory show that the adsorbed water layer is inhomogeneous and the surface is not uniformly covered even at high relative humidity. The impact of the nature of the adsorbed water layer on the surface chemistry of

carbonate and oxide surfaces under ambient conditions will be discussed.

10:40am **SS1-WeM9 The Composition of the Liquid/Vapor Interface of Aqueous Nitrate and Nitric Acid Solutions**, *T.L. Lewis*, Univ. of California, Irvine, *M.A. Brown*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *K. Callahan*, Univ. of California, Irvine, *M. Faubel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *D. Tobias*, Univ. of California, Irvine, *B. Winter*, Hemholtz-Zentrum Berlin für Materialien und Energie, Germany, *J.C. Hemminger*, Univ. of California, Irvine

Nitrate anions become incorporated into sea salt aerosols through the uptake of gas-phase nitric acid in atmospheric aging processes. It has been suggested that photochemical decomposition of nitrate ions in the near surface region of such aerosols leads to OH radical production and subsequent halogen oxidation. However, the concentration of nitrate ions at the surface of aqueous solutions has been a controversial topic in the literature. We obtain a depth profile of the interfacial composition of nitrate anions in aqueous solution in the presence of alkali halide salts. All experiments were performed with XPS on a liquid micro jet and were acquired using tunable synchrotron radiation from the U41-PGM undulator beamline of the BESSY facility in Berlin, where we can vary the photoelectron kinetic energy to obtain depth dependent composition information. Our previous work shows that while nitrate and nitrite anions have a finite concentration at the interface, both prefer bulk solvation. Current results indicate that co-dissolved alkali halide salts in a sodium nitrate solution push the nitrate anion further into the bulk and away from the liquid-vapor interface. A greater effect is seen with increasing concentration of alkali halide as well as increasing size and polarizability of the halide anion. Comparison will be made with MD simulations of the corresponding solutions. In studies of nitric acid, another key component in the atmospheric chemistry of sea salt aerosols, tunable XPS elucidates the depth dependence of undissociated nitric acid. Results show that a higher concentration of undissociated nitric acid is present in the surface region relative to the bulk. Additionally, the relative concentration of undissociated nitric acid increases with increasing nitric acid concentration. These results have significant implications for the chemistry and photochemistry of sea salt aerosols.

11:00am **SS1-WeM10 Investigation of Hydroxyl Dimer Rows Formed by Thermal Dissociation of Water on Cu(110) Surface**, *B.Y. Choi*, *Y. Shi*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Water dissociation on the surface is the first step in many reactions and wetting processes. A fundamental understanding of this process is necessary and applies to various fields, such as corrosion, catalysis, electrochemistry and hydrogen generation. Thermally dissociated water molecules on an oxygen precovered Cu(110) surface are investigated using scanning tunneling microscopy (STM) at low temperature. Chain structures of elongated molecules are obtained by dosing water on an oxygen precovered Cu(110) at 77K followed by annealing to ~180K. Density functional theory calculations reveal that the elongated molecular shapes are made of two hydrogen bonded OH molecules which form a dimer by tilting one OH to the other¹. The weak interaction between dimers gives rise to the changes in shape of the cluster. We propose that this structural variation is the result of molecular fluctuations and from the interaction with atomic hydrogen produced by water dissociation. Switching between the different dimer shapes can be accomplished by exciting the OH-stretch mode with tunneling electrons.

¹T. Kumagai et al Phys. Rev. B 79, 035423 (2009)

11:20am **SS1-WeM11 Key Processes of Ice-Multilayer Evolution during Growth and Annealing Studied with STM**, *K. Thürmer*, *S. Nie*, *N.C. Bartelt*, Sandia National Laboratories

Although extensive research has been aimed at the structure of ice films [1], important details of the morphology evolution, especially for films in the nm-thickness range, have remained elusive. Our capability to image up to 30 molecular layers of ice with STM [2], enables us to track the film evolution during growth and annealing. In particular, we investigate the role of new-layer nucleation and surface self-diffusion.

As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120K and ~150K. At 140K and a mean film thickness of ~1nm the film consists of 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. Analyzing the annealing behavior of these crystallites we find [3] that the rate at which new layers nucleate, and not surface diffusion, determines how fast individual crystallites equilibrate. The resistance to nucleate new layers even during deposition has a surprising effect on thicker films: The deposited water attaches preferentially to growth spirals

around screw dislocations, promoting the formation of metastable cubic ice [2].

Finally, we report the first measurements of surface self-diffusion on ice. Using uniform 5-nm-thick ice films (grown at 145K) as templates, we deposited a fraction of a monolayer of water at 115K to create metastable arrays of 2D-islands. By quantifying the Ostwald ripening of these arrays upon annealing between 115 and 135 K, we extract temperature-dependent diffusion rates and determine the activation energy for surface self-diffusion to be (0.4±0.1) eV [4].

[1] A. Verdagner, G. M. Sacha, H. Bluhm, and M. Salmeron, Chem. Rev. **106**, 1478 (2006).

[2] K. Thürmer and N. C. Bartelt, Phys. Rev. B **77**, 195425 (2008).

[3] K. Thürmer and N. C. Bartelt, Phys. Rev. Lett. **100**, 186101 (2008).

[4] S. Nie, N. C. Bartelt, and K. Thürmer, Phys. Rev. Lett. **102**, 136101 (2009).

11:40am **SS1-WeM12 Structure of Ultra Thin Water Films on Ruthenium**, *S. Maier*, *I. Stass*, Lawrence Berkeley National Laboratory, *J.I. Cerda*, Instituto de Ciencia de Materiales de Madrid, Spain, *P.J. Feibelman*, Sandia National Laboratories, *M. Salmeron*, Lawrence Berkeley National Laboratory

The structure and chemistry of water at surfaces and interfaces is an unresolved and fundamental topic in many areas of science and technology such as catalysis, electrochemistry and environmental sciences. We use low temperature scanning tunneling microscopy in combination with DFT calculations to study the structure and reactions of ultra thin water films on Ru(0001) at the molecular scale.

We present new results on the formation of mixed water-hydroxyl structures following partial dissociation, observed above 130K. We found that the hydrogen produced during partial dissociation can be trapped in the interior of the hexagonal unit cell of the water hydroxyl structures and outside of the hexagons which is thermodynamically more stable. In addition, we studied the structure of water beyond the first layer and discovered that the hexagonal network of the second layer is surprisingly rotated 30° with respect to the first on Ru(0001) as well as on Pd(111). This rotation leads to a bonding structure between the water layers that significantly deviates from the conventional ice-like water model on hexagonal metals. We propose models for this novel structure of the first two water layers based on DFT calculations. Beyond the second water layer, a transition to the growth of compact ice clusters was found.

Surface Science

Room: N - Session SS2-WeM

Surface Chemistry and Dynamics

Moderator: C.E. Sykes, Tufts University

8:00am **SS2-WeM1 Adsorption of Xenon on Vicinal Copper Surfaces**, *B. Holsclaw*, *A.J. Gellman*, Carnegie Mellon University

The adsorption of xenon was studied on Cu(111), Cu(221), Cu(643), and Cu(653) using temperature programmed desorption (TPD) of xenon and ultraviolet photoemission of adsorbed xenon (PAX). These experiments were performed to study the atomic and electronic structure of step-kinked, chiral copper surfaces. Xenon TPD and PAX were performed in an attempt to distinguish terrace, step-edge, and kink adsorption sites by adsorption energy (TPD) and local work function differences (PAX). The different adsorption sites could not be clearly differentiated using xenon TPD due to the complex behavior of xenon on these surfaces. Comparison of TPD spectra of *R*-3-methylcyclohexanone (*R*-3-MCHO) previously performed¹ on stepped and kinked copper surfaces suggests clear differences between Cu(643) and Cu(653) that are not apparent using xenon TPD. However, unique features of xenon adsorption on different copper surfaces were visually and numerically distinguishable using the PAX method. The PAX experiments on the copper surfaces demonstrate local work function differences between kink and step surface sites as well as step and terrace sites. A data fitting model was developed to analyze the PAX data for all four copper surfaces simultaneously. Kink sites were found to have a lower local work function than step sites, and steps, in turn, had a lower local work function than terrace sites. Step/kink adsorption of xenon is favored (for all surfaces studied at 50-70 K) at low coverages of xenon, but these sites do not saturate until monolayer coverage is reached. The results of this research provide several observations regarding the adsorptive behavior of xenon on vicinal copper surfaces.

¹Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J., Enantioselective separation on a naturally chiral surface. *Journal of the American Chemical Society* **2004**, 126, (45), 14988-14994.

8:20am SS2-WeM2 Effect of Surface Order and Thickness on the Adsorption Mechanism of NO on FePc. *S.R. Bishop, N. Tran, A.C. Kummel*, University of California, San Diego

The diverse electronic properties, chemical and thermal robustness, and ease of deposition (spin coating and organic molecular beam epitaxy) make Metallophthalocyanine (MPc) materials an attractive and economical candidate for use in chemical sensors. The purpose of this study is to obtain an atomic level understanding of the fundamental mechanisms in which analytes interact with MPc thin films. MPc thin films investigated include ordered monolayer FePc, ordered multilayer FePc, and quasi-amorphous tetra-*t*-butyl FePc multilayer thin films. These experiments were further supported with density functional theory (DFT) of NO adsorption on FePc via simulated potential energy diagram. Exploration of how surface order and thickness affects NO adsorption was performed via King and Wells sticking measurements. The unique sticking profile features a sharp, downward spike, representing a short saturation time. For monolayer and ordered multilayer FePc/Au(111), NO adsorption onto FePc saturates at 3% of a monolayer suggesting that the final chemisorption site is confined to the iron metal centers. Furthermore, the saturation coverage is only 2% for the quasi-amorphous multilayer. The reduced saturation coverage in comparison to ordered FePc is attributed to the lower packing density of the tert-*t*-butyl FePc. At low surface temperature and low incident beam energy, the initial sticking probability is as great as 40% and decreases linearly with increasing beam energy and surface temperature. This is consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the organic periphery followed by diffusion to the Fe metal center, precursor-mediated chemisorption. For the multilayer ordered flat-lying film, the sticking probabilities are greater in comparison to the monolayer for the same incident beam energy and surface temperature. More efficient trapping onto the ordered multilayer film is consistent with NO having improved mass-matching with the multilayer FePc surface compared to monolayer. In addition, computations suggest that there are multiple available physisorption sites available within the organic periphery of the FePc films. The results strongly suggest the analyte adsorbs via a multiple pathway precursor-mediated chemisorption mechanism. A current study focuses on the analyte adsorption onto a totally amorphous film. MPc forms a β -polymorph on SiO₂ substrates which are no longer flat-lying, and planned sticking measurements of NO interaction with amorphous FePc will complete the study of the effect of surface order on analyte adsorption.

8:40am SS2-WeM3 Interfacial Bonding of Thiophene and Aromatic Isocyanide on Au(111). *J. Zhou, Y. Yang, SUNY Stony Brook, P.J. Liu, N. Camillone*, Brookhaven National Laboratory, *M. White*, Brookhaven National Laboratory & SUNY Stony Brook

The electronic structures of thiophene and 1,4-phenylene diisocyanide (PDI) adsorbed on Au(111) are investigated by two-photon photoemission (2PPE) spectroscopy and density functional theory (DFT) calculation. The adsorption of thiophene lowers the work function by 0.88 eV for Au(111) exposed to 4.0 L thiophene, due to the electron donation from the thiophene to the substrate. With thiophene adsorbed on Au(111), a localized σ^* state forms with increasing thiophene exposure on Au(111). This state is attributed to the σ^* antibonding orbital of a Au-S bond and is evidence of an orientational phase transition of adsorbed thiophene. For PDI adsorbed on Au(111), a bonding state located at 0.8 eV below the Fermi level forms at the interface. The temperature dependence of work function change of PDI/Au(111) provides an evidence for molecular crystallization on the surface. Adsorption of 1 monolayer of PDI on Au(111) lowers the work function by 0.25 eV. Upon annealing to 300 K, the work function decreases by 1.45 eV due to amplified charge transfer or dipole effects which induced by the formation of a crystallized layer.

9:00am SS2-WeM4 Identification of C₂H_x Intermediates on Pt(111) through the Combined Use of Low Temperature Scanning Tunneling Microscopy and Reflection Absorption Infrared Spectroscopy. *T. Okada, Y. Kim, M. Kawai*, RIKEN, Japan, *M. Trenary*, University of Illinois at Chicago

Various C₂H_x surfaces intermediates formed through the thermal decomposition of acetylene and ethylene on the Pt(111) surface were identified and their stabilities characterized through complementary studies using the techniques of low temperature scanning tunneling microscopy (LT-STM) and reflection absorption infrared spectroscopy (RAIRS). By providing high-resolution vibrational spectra of surface species, RAIRS data is highly sensitive to the chemical identity of those species. However, it does not provide information on the relative coverages of adsorbed molecules and many important stable intermediates are invisible to RAIRS. In contrast, with a LT-STM operated at 4.7 K, individual molecules are

observable and their absolute coverages are readily obtained simply by counting, yet their chemical identities cannot be directly determined from the STM images alone. In the case of acetylene, both RAIRS and LT-STM indicate that it adsorbs in a single form at low temperature in which the CC bond is positioned over a three-fold hollow site, and that the interaction with the surface occurs through both di- σ and π bonding. On warming to 250 K in the presence of coadsorbed hydrogen, RAIRS provides strong evidence for the partial hydrogenation of acetylene to form an adsorbed vinyl (CHCH₂) species. The LT-STM images following a 250 K anneal in the presence of coadsorbed hydrogen show a marked increase in the coverage of a species that is identified as vinyl, based on the RAIRS results. Both techniques indicate that adsorbed acetylene is stable up to 300 K. A third species, in addition to adsorbed acetylene and vinyl, is also observed with the LT-STM after a 300 K anneal, which is identified as vinylidene, CCH₂. However, the RAIRS evidence for a vinylidene species is not definitive. In the case of ethylene adsorption at low temperature, RAIRS provides clear evidence for a di- σ bonded form of ethylene at low temperatures that converts to ethynyl at 280-420 K. The LT-STM images show that ethylene exists in both π -bonded and di- σ bonded forms at low temperature and that the two forms can be easily interconverted using electron pulses from the STM tip. On the basis of RAIRS experiments, it was found that surface carbon formed through the complete dehydrogenation of acetylene could be hydrogenated to form ethynyl (CCH₃), from which it was inferred that the surface carbon was in the form of C₂ molecules. A form of surface carbon that can be hydrogenated to ethynyl was also identified with LT-STM. Other surface species that have been investigated with the two techniques include ethynyl (CCH), ethylidene (CHCH₂), and methylidyne (CH).

9:20am SS2-WeM5 Dehydrogenation of Single Ammonia Molecules on Ruthenium. *I. Stass, S. Maier, M. Salmeron*, Lawrence Berkeley National Laboratory

Ammonia (NH₃) can be potentially used for hydrogen storage, because the dissociation of ammonia molecules generates hydrogen. Although Ruthenium is the best elementary metallic catalyst for ammonia synthesis, the exact reaction mechanisms at the atomic scale of both synthesis and dissociation over the Ruthenium surface have yet to be understood. Previously, the dehydrogenated products were obtained by annealing the sample and characterized by spectroscopic methods.

We studied the dehydrogenation of single ammonia molecules adsorbed on a Ru(0001) surface, by means of scanning tunneling microscopy (STM) at low temperature. The sudden change in tunneling current during the dissociation process allows us to study the dissociation mechanism and rate of single molecules in detail. We observe the different dehydrogenation steps after selectively applying voltage pulses in the order of a few volts between STM tip and an adsorbed ammonia molecule. The various dissociation products show a distinct imaging contrast. Together with the assignment of the adsorption site, this leads to the identification of the dissociation products. We will discuss to what extent electron induced and electric field driven processes, respectively, are affecting the dissociation mechanism of ammonia and its dissociation products.

9:40am SS2-WeM6 The Ca / MEH-CN-PPV Interface: Ca Adsorption Calorimetry, LEIS and XPS. *J.C. Sharp, J.H. Baricuatro*, University of Washington, *F. Bebensee, H.-P. Steinrueck, J.M. Gottfried*, Universitaet Erlangen-Nuernberg, Germany, *C.T. Campbell*, University of Washington

Conjugated polymers are of interest for use in photovoltaics and OLEDs because of the tunability of their band gap and ease of processing them into devices. Poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene) (MEH-CN-PPV) has high photoluminescence efficiency and thus has potential use in OLEDs. The interaction between the conjugated polymer and metal electrode is critical to the performance of these devices. The energetics and structure of calcium growth on MEH-CN-PPV was studied using adsorption microcalorimetry and low-energy ion scattering spectroscopy (LEIS) in ultrahigh vacuum. At 300 K the integrated Ca LEIS peak area grew slowly until ~1.5 ML and the rate of growth increased until a continuous film of Ca was formed by ~15 ML. The slow initial growth rate is due to calcium diffusing subsurface. After ~1.5 ML, Ca forms 3-D islands on the surface. At 130 K, the transitions from subsurface diffusion to 3D cluster growth to film formation occur at lower coverages. The initial heat of adsorption of Ca on MEH-CN-PPV at 300 K is 436 kJ/mol. The heat of adsorption increases to 464 kJ/mol at ~0.1 ML and then decreases to the heat of sublimation of Ca by 4 ML. Similar behavior is seen at 130 K with the initial heat of adsorption being 326 kJ/mol and increasing to 331 kJ/mol at ~0.1 ML and decreasing to the heat of sublimation already by 1.25 ML. The sticking probability (S) at 300 K was 0.70 initially and increased to 0.75 at ~0.1 ML of Ca coverage. After ~0.1 ML, S decreased to 0.64 by ~1.5 ML, then gradually increases to unity. The initial sticking probability at 130 K was 0.92 and increased toward unity. The thermodynamic, sticking

and growth behavior below 1.5 ML, where Ca is interacting strongly with specific adsorption sites on the polymer, will be discussed

10:40am **SS2-WeM9 STM Tip Induced Surface Reactions on TiO₂(110)**, *D.V. Potapenko, R.M. Osgood*, Columbia University

Chemistry on the surfaces of photocatalytic materials, including TiO₂, is driven by the charge carriers that are created in the bulk of the catalyst by light adsorption. The tip of a scanning tunneling microscope may serve as an alternative source of both free electrons and holes in a semiconductor. We have studied adsorption and tip-induced surface chemistry of 4-bromobiphenyl on the TiO₂(110) surface. The adsorbed molecules could be identified in the STM images at the limit of low coverages. The response of the surface to the adsorbed substance was characterized with in situ temperature program desorption. Passing the electric current from the STM tip through molecules caused dissociation of the molecules as was indicated by the changes in the STM images. We report on the conditions of the tip-induced chemistry and propose mechanistic explanation of the observed phenomena. An important follow on experiment to this work will be to examine reactions on nanocrystal TiO₂.

11:00am **SS2-WeM10 H₂O Interaction with Oxygen Adatoms on TiO₂(110)**, *Y. Du, A. Deskins, Z. Zhang, Z. Dohnalek, M. Dupuis, I. Lyubinetsky*, Pacific Northwest National Laboratory

Water and oxygen interactions on the catalytically important TiO₂ surfaces have attracted great interest from both fundamental and technological points of view. In this work, surface chemistry of water on oxidized TiO₂(110) surfaces is investigated by scanning tunneling microscopy studies and density functional theory calculations. We show that oxygen adatoms (O_a), generated during oxygen dissociation, alter the water dissociation and recombination chemistry through two distinctive pathways. Depending on whether H₂O and O_a are on the same or adjacent Ti⁴⁺ rows, O_a facilitates H₂O dissociation and proton transfer to form a terminal hydroxyl pair, positioned along or across the Ti⁴⁺ row, respectively. The latter process involves proton transfer through a bridging oxygen atom where H₂O is considered to be in a "pseudo-dissociated" state. In both pathways, the reverse H transfer results in H₂O reformation and statistical O scrambling, as manifested by an apparent along- or across-row motion of O_a's.

11:20am **SS2-WeM11 Sulfur Adsorption on Ag(111) and Ag(100): Structures and Surface Dynamics**, *D.-J. Liu, M. Shen, S. Russel, C.J. Jenks, J.W. Evans, P.A. Thiel*, Iowa State University

Exposure to sulfur (S) of Ag(111) and Ag(100) produces ordered surface structures as observed by STM. On Ag(111), a self-organized dot-row structure forms at around 200 K [1]. The dots, likely Ag₃S₃ clusters, can rearrange and form other more closed-packed structures at higher S coverages. On Ag(100) at 230 K, a $\sqrt{17}$ reconstruction structure appears for S coverage above 0.25 ML, together with a p(2x2) structure. STM studies also reveal that exposure to sulfur generally accelerates coarsening of 2D Ag nanoislands preformed on the surface by Ag deposition. For Ag(111), since steps serve as sinks for S, dramatic enhancement of Ostwald ripening only occurs above a threshold (step saturation) coverage of S [2]. For Ag(100), Ostwald ripening is activated with a rate increasing gradually with increasing S coverage. Possible acceleration mechanisms include AgnSm complex mediated mass transport, or S-catalyzed attachment-detachment. We perform a detailed analysis of the stability and formation energies of various structures and Ag-S complexes using DFT. Many aspects of the observed structures and mechanisms for mass transport during coarsening are elucidated based on these DFT energetics together with kinetic modeling.

[1] Shen *et al.* J. Phys. Chem. C **112** (2008) 4281

[2] Shen *et al.* J. Chem. Phys. **130** (2009) 094701

11:40am **SS2-WeM12 Ionicity of Adsorbates: Dependence on Coverage, Site, and Substrate**, *P.S. Bagus, University of North Texas, Ch. Wöll, Ruhr-Universität Bochum, Germany, A. Wieckowski, University of Illinois at Urbana-Champaign*

We present detailed theoretical analyses of nominally anionic Iodine and nominally cationic Cs adsorbed on Cu(111) and Pt(111) surfaces. We consider the consequences of the coverage, the choice of on-top or three-fold sites, and the differences between Cu and Pt substrates on the degree of ionicity and on other properties of the interaction. This work extends our earlier studies of I and Cs on Cu(111)¹ and of I/Pt(111).² There we demonstrated that, although both Cs and I were dominantly ionic adsorbates, the properties of the adsorption, including work function changes, $\Delta\Phi$, and photoemission binding energy shifts, ΔBE , depended on other factors besides the adsorbate ionicity. However in this earlier work, only a single I or Cs adsorbate was explicitly treated and we neglected both direct and indirect, substrate mediated, adsorbate-adsorbate interactions. Now, we use models where several adsorbates are included, thus explicitly

modeling lower and higher coverages. In particular, we examine whether the coverage dependent departures from ideal ionicity are different for cations and anions. Furthermore, we examine how $\Delta\Phi$ depends on the adsorbate-adsorbate interaction and compare our predictions with measurements of $\Delta\Phi$ as a function of coverage. This is relevant for the modification of charge transport barriers, which is key for the design of organic electronics.³ The distance of I above Pt(111) is quite different for on-top and three-fold sites,² which has important consequences for $\Delta\Phi$ and ΔBE . Here, we examine the generality of different heights of ionic adsorbates at these sites and how this difference is affected by the sign of the ionicity and the substrate. Our theoretical methodology uses wavefunctions for cluster models of the surface since this allows us to determine the quantitative importance of the individual physical and chemical mechanisms that contribute to the interaction. Our present work marks the first time that these methods have been applied to study the influence of coverage for halogen and alkali metal adsorbates.

¹P. S. Bagus, D. Käfer, G. Witte, and C. Wöll, Phys. Rev. Lett., **100**, 126101 (2008).

²P. S. Bagus, C. Wöll, and A. Wieckowski, Surf. Sci. **603**, 273 (2009).

³G. Witte, S. Lukas, P. S. Bagus, and C. Wöll, Appl. Phys. Lett., **87**, 263502 (2005).

Wednesday Afternoon, November 11, 2009

Surface Science

Room: M - Session SS1-WeA

Water/Surface Interactions & Environmental Chemistry II

Moderator: V. Grassian, University of Iowa

2:00pm **SS1-WeA1 Towards Understanding the Formation of Water in the Interstellar Medium**, V.L. Frankland, M.P. Collings, M.R.S. McCoustra, Heriot-Watt University, UK

Exposed to the harsh radiation fields of interstellar space, few molecules can escape photodestruction. However, the vast clouds of gas and dust that accumulate in the gulfs of space between the stars (known as the interstellar medium) have been observed to contain more than 120 different molecular species¹. The low temperature (10-100 K) and pressure (10^{-14} mbar) conditions within the interstellar medium limit the range of viable gas-phase reactions resulting in the gas-phase chemistry alone being insufficient to explain the observed abundances of some key chemical species (for example, H₂ and H₂O). Dust grains provide a surface on which adsorbed species can react² and hence an alternative pathway to key interstellar molecules. Indeed, this has been proven for the efficient formation of H₂ both experimentally³⁻⁶ and computationally⁷⁻⁹.

Surface chemistry within an ultrahigh vacuum chamber is being used to explore the surface irradiation reactions of O on a range of astrophysically relevant surfaces using atomic beam methods. In these experiments, the products are identified using temperature programmed desorption. The results of the experiments are interpreted using kinetic analysis of a simple surface mechanism. Analogous experiments will be conducted using an atomic H beam. The ultimate aim of this research will be to combine the two beams to study *in situ* H₂O formation on a grain surface.

References

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- 8) N. Katz, I. Furman, O. Biham, V. Pirronello, G. Vidali, *Astrophys. J.*, 1999, **522**, 305
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2:20pm **SS1-WeA2 Photon- and Electron-stimulated Desorption from Laboratory Models of Interstellar Ice Grains**, J.D. Thrower, A.G.M. Abdulgalil, M.P. Collings, M.R.S. McCoustra, Heriot-Watt University, UK, F.J.M. Rutten, Keele University, UK

Dense molecular clouds, in our own and other galaxies throughout the Universe, are the seats of evolution in the present day Universe. New stars and their planetary systems are born in such environments from the chemically rich soup of gas and icy dust from which these environments are made. In the last decade or so, astronomers have turned to the surface science community to help explain the role played by physical and chemical processes in coupling of the gas and solid (dust grain) phases in these crucially important regions of space.

We have recently been investigating one key aspect of that gas-grain interaction; the role played by non-thermal (photon- and low energy electron-driven) processes in returning components of the icy grain mantle to the gaseous interstellar medium. Ultrathin layers of predominantly water (H₂O) ice grow reactively on dust grains; such layers can accumulate adsorbed volatiles such as carbon monoxide (CO) from the gaseous interstellar medium and are observed with sufficient ease in the infrared to be mapped. Indeed such icy mixtures are firmly believed to be the home of chemical evolution in these dense environments as the simple ices (H₂O, CO, NH₃ etc.) are converted by a combination of thermal and non-thermal processes into more complex species (e.g. CO₂, CH₃OH, CH₃NH₂ etc.). Further processing of these complex icy mixtures may lead to the formation

of prototypical molecules which may, following exogenous delivery to a nascent planet, provide the raw materials for biological evolution. However such a drive towards increasing chemical complexity takes time; time in which competition from non-thermal desorption processes may in fact remove the icy mantle from its substrate exposing the fragile molecular contents to the harsher environment of the gaseous interstellar medium. We describe preliminary studies of both photon- and low energy electron-driven desorption from a model interstellar ice deposited on model grain surfaces under UHV conditions. We will report on the rates of desorption mediated by photon- and electron-stimulated interactions and, where known, outline the dynamical consequences of such desorption.

2:40pm **SS1-WeA3 Structure-Property Relationships of Water Interfaces 200° Beyond the Boiling Point**, S. Putnam, L. Gschwender, Thermal and Materials Sciences Branch - WPAFB

In cooling technologies that utilize the latent heat of vaporization (e.g. pool boiling and spray cooling), knowledge of the critical heat flux is "critical." Beyond the critical heat flux, a continuous vapor layer forms at the solid-liquid interface that impedes heat transfer. The formation of this chaotic, thermally-resistive vapor layer" is well known. However, our recent research has demonstrated that a new, unique, and stable water interface is formed beyond the critical heat flux for surface temperatures 100+ degrees above the boiling point. At this point, film boiling stops, forming a smooth, highly light reflective, high surface energy water interface that further impedes heat transfer. We present our efforts in correlating the thermal, mechanical, and structural properties of this unique water interface using high-speed imaging, Raman spectroscopy, and numerical modeling. Critical heat flux data as a function of vapor pressure is also presented for water boiling on patterned surfaces of carbon nanotubes and nanowire whisker arrays.

3:00pm **SS1-WeA4 Proton and Water Self-diffusion in Thin Layers of Amorphous Solid Ice Studied by FTIR and DFT Calculations**, P.E. Uvdal, J.E. Blomquist, Lund University, Sweden

We have studied the H/D exchange in both two- and three-dimensional thin layers of amorphous solid ice using infrared vibrational spectroscopy. Intact molecules are grown in a layer by layer fashion, on Cu(100), allowing the formation of isotopically uniform sandwiched layers at 84 K. By careful pretreatment of the surface we can control the proton diffusion, thereby allowing for a separation and a characterization of the two diffusion processes. The role of the Grothuss mechanism for the observed H/D exchange will be discussed. Using infrared vibrational spectroscopy we can monitor the isotopic mix of water molecules both at the ice surface as well as in the solid ice. A detailed understanding of the vibrational data is obtained with the aid of DFT cluster calculations.

4:00pm **SS1-WeA7 Surface Science Studies of Environmentally Relevant Chemistry on Some Metal Sulfide and Oxide Minerals**, D.R. Strongin, Temple University

INVITED

Studies are presented that investigated environmentally relevant chemistry on pyrite (FeS₂), birnessite (MnO₂), and nanocrystalline ferrihydrite. Photoelectron spectroscopy, in situ atomic force microscopy, and in situ infrared spectroscopy studies will be presented that address the oxidation of pyrite, arsenite adsorption on birnessite, and carbonate formation of ferrihydrite. Selected results from these studies will bring forward important issues related to the understanding of complex environmental chemistry occurring on mineral surfaces. In the arsenite/birnessite circumstance, for example, batch reaction measurements determined the extent of the conversion of the arsenite to arsenate and the amount of Mn(II) formed during this reductive dissolution process. Atomic force microscopy (AFM) investigated morphology changes during the reactions associated with birnessite as well as the nature of any precipitate phases by using phase imaging. The microscopy was complemented by X-ray photoelectron spectroscopy (XPS) that was able to determine the relative distribution of Mn(IV), Mn(III) and Mn(II) after reaction with As(III). Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was also used to determine the nature of the arsenic-species on the Mn oxide and oxyhydroxide surfaces.

4:40pm **SS1-WeA9 Water Growth on a Hydrophobic Substrate: Observation of a Metastable, Two-Layer Crystalline Ice on Graphene**, G.A. Kimmel, J. Matthiesen, Pacific Northwest National Laboratory, M. Baer, Ruhr-Universität Bochum, Germany, C. Mundy, N.G. Petrik, R.S. Smith, Z. Dohnálek, B. Kay, Pacific Northwest National Laboratory

The structure of water at interfaces is crucial for processes ranging from photocatalysis to protein folding. Here, we investigate the structure and lattice dynamics of two-layer crystalline ice films grown on a hydrophobic

substrate – graphene on Pt(111) – with low energy electron diffraction, reflection-absorption infrared spectroscopy, rare-gas adsorption/desorption, and *ab-initio* molecular dynamics. Unlike hexagonal ice, which consists of stacks of *puckered* hexagonal “bilayers”, this new ice polymorph consists of two *flat* hexagonal sheets of water molecules in which the hexagons in each sheet are stacked directly on top of each other. Such two-layer ices have been predicted for water confined between hydrophobic slits, but not previously observed. Our results show that the two-layer ice forms even at zero pressure at a single hydrophobic interface by maximizing the number of hydrogen bonds at the expense of adopting a non-tetrahedral geometry with weakened bonds.

5:00pm **SS1-WeA10 SrTiO₃(001) Surface Structure Stabilization Via Water Mediation**, A.E. *Becerra-Toledo*, D.M. *Kienzle*, L.D. *Marks*, Northwestern University

Strontium titanate, SrTiO₃, has been largely studied as the quintessential model system for perovskite oxides. In the field of surface science, the presence of multiple cation valence states has allowed for insights into the stabilization mechanisms in mixed-metal oxides. Multiple SrTiO₃ surface structures have been conclusively described at the atomic scale, which lets us go beyond bulk-like caricature descriptions of oxide surfaces. In turn, this allows for a more realistic study of the interaction of oxide surfaces with foreign species such as water, whose ubiquity makes such analysis inescapable.

Density functional theory (DFT) calculations were performed to study the surface energetics of several observed and theoretical SrTiO₃(001) surface reconstructions, both dry and with chemisorbed water. A repeated slab configuration was used to model all surface structures, which include not only bulk-like truncations, but also the 2x1, c(4x2), ($\sqrt{13}\times\sqrt{13}$)R33.7° reconstructions, as well as the theoretically predicted low-energy ($\sqrt{2}\times\sqrt{2}$)R45° structure. The use of an augmented plane wave plus local orbital (APW+lo) basis, coupled to the full-electron potential implementation, accurately reflects the character of single-particle wavefunctions. The TPSSh hybrid meta-GGA exchange-correlation functional [Tao et al., PRL 91,146401 (2003)] was employed, which allows for an improved treatment of strongly correlated systems. Both the molecular and dissociative water adsorption modalities were taken into account.

Our analysis suggests that water mediation is responsible for the fact that the thermodynamically favorable ($\sqrt{2}\times\sqrt{2}$)R45° structure [Warschkow et al., Surf.Sci. 573, 446 (2004)] has never been detected while other reconstructions of identical stoichiometry and significantly higher surface energy, such as the 2x1, have been readily observed. In the latter, the adsorption of water is much more favorable, which insinuates that the formation of the ($\sqrt{2}\times\sqrt{2}$)R45° reconstruction is kinetically limited if there is any exposure to water vapor. Several experimental results back up this observation.

5:20pm **SS1-WeA11 Water Adsorption on O(2x1)-Ru(0001)**, S. *Maier*, I. *Stass*, M. *Salmeron*, Lawrence Berkeley National Laboratory

We studied the adsorption of water on the O(2x1) -Ru(0001) surface at submonolayer coverage by low temperature scanning tunneling microscopy. We found that water reconstructs the oxygen layer from a linear configuration to a honeycomb structure with the water molecules incorporated inside, confirming a model previously proposed by Gladys et al. based on XPS measurements [1]. In addition, we found that water monomers inside the oxygen hexagons can rotate through interaction with the tip, while dimers are more stable.

[1] M.J. Gladys et al. PRB 78, 035409 (2008).

5:40pm **SS1-WeA12 Structure and Dynamics of Liquid Water on Surfaces from Ab Initio Molecular Dynamics: Graphene/Water and Alumina/Water**, P. *Huang*, E. *Schwegler*, Lawrence Livermore National Laboratory

Many important surface phenomena occur under aqueous conditions, where water plays a significant but poorly understood role in interfacial structure and reactivity. Atomic-scale information at solid/water interfaces is notoriously difficult to unravel, and thus simulations are an essential complement to experimental efforts. To date, such simulations typically rely on simple, empirical models for interatomic interactions. However, there is a great deal of ambiguity in the parameterization of these potentials; often they are fitted to bulk properties, and the transferability to complex interfacial systems is unclear. Here, we report atomic-scale simulations of solid/water interfaces via *ab initio* molecular dynamics, where interatomic interactions are derived on-the-fly from density functional theory. Unlike empirical models, this approach is generally applicable to both bulk and interfacial environments, without input from experiment. Two prototype

examples are considered: graphene/water as a model hydrophobic surface, and alumina/water as a model oxide surface. In both cases, a bulk-like liquid water layer at ambient conditions is explicitly included. We examine interfacial structure and dynamics, relate these to spectroscopic observables (infrared spectroscopy, nuclear magnetic resonance). Comparison to predictions from common empirical potentials is given in order to gain insight into when such models fail, and how they can be improved.

Surface Science

Room: N - Session SS2-WeA

Surface Physics, Single Particle Imaging

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-WeA1 Dynamics of Alkali Metals Adsorbed on Cu(111) at Low Density using High Resolution ³He Spin-Echo Spectroscopy**, D.J. *Ward*, A.P. *Jardine*, H.J. *Hedgeland*, W. *Allison*, J. *Ellis*, University of Cambridge, UK

Alkali atoms at surfaces show unexpected behaviour arising from the strong interadsorbate forces and coupling of electronic and nuclear motion [2,3]. In the present work we present new results giving additional insight into both the dynamics and the scattering.

High resolution quasielastic helium atom scattering (QHAS) experiments provide a unique tool to study adsorbate dynamics[1] since ³He spin-echo measurements give the surface correlation in time through the intermediate scattering function (ISF), I($\Delta K, t$). The functional form of the ISF has a well defined analytic form for simple systems, however for real systems the form is typically complex and challenging to predict. For example the shape of the ISF can take a multifunctional form due to summation effects from multiple species or clusters moving with the same or different modes, and a convolution effect from differences in the local appearance of the potential energy landscape to the adsorbate for the length scale under study.

Previous investigations of the diffusion of alkali metals on metal surfaces have revealed unexpected phenomena. For sodium on Cu(100), a 'new' mode of aperiodic motion, perpendicular to the surface, was discovered[2]. For caesium, the observed dynamics on the same surface were found to be qualitatively different to sodium[3], indicating a critical balance of adsorbate-substrate and adsorbate-adsorbate interactions, determining the behaviour for each adsorbate.

In this work we present detailed helium-3 spin-echo QHAS measurements of the dynamics of sodium adsorbed on Cu(111) at low to moderate coverages. We observe a QHAS broadening with the presence of a complex lineshape which shows a momentum transfer variation. The functional form is compared with theoretical models[4] for different potential energy landscapes. The variation of the QHAS broadening with temperature and momentum transfer are studied to access information on the dynamic phenomena on the Cu(111) surface, exploring in particular the generality of perpendicular motion, and changes in the adsorbate-substrate/adsorbate-adsorbate force balance.

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2:20pm **SS2-WeA2 MORTON S. TRAUM AWARD FINALIST: Direct Observation of Hydrogen-Bond Exchange within a Single Water Dimer**, T. *Kumagai**, M. *Kaizu*, H. *Okuyama*, Kyoto University, Japan, S. *Hatta*, T. *Aruga*, Kyoto University, JST-CREST, Japan, I. *Hamada*, Y. *Morikawa*, Osaka University, Japan

The nature of the hydrogen bond is related to many physical, chemical and biological processes. The structure and dynamics of water dimers, which consist of hydrogen-bond donor and acceptor molecules, have been subjects of extensive research as a prototype of much more complex hydrogen-bonding systems. The water molecules in a free water dimer rearrange the hydrogen bond through quantum tunneling among equivalent structures [1]. Recently, we reported the visualization in real space of hydrogen-bond exchange process governed by quantum tunneling within a single water

* Morton S. Traum Award Finalist

dimer adsorbed on a metal surface with a low-temperature scanning tunneling microscope (STM) [2].

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM operating at 6 K. The Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H₂O or D₂O gases via a tube doser below 20 K. We conducted the experiments at very low coverages, where water molecules exist mainly as isolated monomers and dimers on the surface.

A water dimer is characterized by its bi-stable fluctuating image due to the interchange motion of the hydrogen-bond donor and acceptor molecules. The STM image of the dimer shows dramatic change upon substitution with heavy water. The interchange motion of (D₂O)₂ is much slower than that of (H₂O)₂. The interchange rate was determined to be $(6.0 \pm 0.6) \times 10^{-1}$ s⁻¹ for (H₂O)₂ and 1.0 ± 0.1 s⁻¹ for (D₂O)₂ by monitoring the interchange events in real time. The large isotope effect (~60) suggests that the rate-limiting process involves quantum tunneling. In addition, DFT calculation revealed that the barrier of the interchange on Cu(110) is 0.24 eV. This cannot be overcome via mere thermal process at 6 K, which corroborates that the interchange proceeds through tunneling.

Furthermore, the interchange rate is enhanced upon excitation of the intermolecular mode that correlates with the reaction coordinate. While the interchange motion is intrinsic at low bias voltage, as indicated by negligible tip effect, it becomes tip assisted at voltages above 40 mV. The threshold voltage is determined to be 45 ± 1 (41 ± 1) mV for H₂O (D₂O) dimers. The barrier for the interchange (0.24 eV), however, much larger than the energy transferred from a tunneling electron (45 mV). Consequently, we propose that the interchange tunneling is assisted by vibrational assisted tunneling process.

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[2] T. Kumagai *et al. Phys. Rev. Lett.* 100, 166101 (2008).

2:40pm SS2-WeA3 Single Molecule Assembly, Chirality and Catalysis, C.E. Sykes, Tufts University **INVITED**

Self-assembled monolayers (SAMs) offer many useful applications in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. Thioethers are more resilient to oxidation than thiols and offer the potential for control over nanoscale assembly in two dimensions parallel to the surface. Low-temperature scanning tunneling microscopy (LT-STM) data demonstrates that thioethers form large, very well ordered domains with little or no defects that cover areas >1,000nm². In contrast to alkane thiol assembly on the same surface, thioethers do not lift the Au {111} herringbone reconstruction. This feature facilitates defect-free thioether assembly which is not disrupted by etch-pit formation that alkane thiol SAMs suffer from. These data suggest the potential use of thioethers for a variety of self-assembly applications that require very perfect assembly and control over molecular spacing parallel to the surface.

Thioethers also constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a mechanism that involves excitation of a C-H stretch. Forming ordered arrays of molecular rotors may provide entirely new approaches to signal processing, sensing, and energy modulation. For this application, an array of dibutyl sulfide rotors has been formed on a Ag/Cu{111} surface alloy. Molecular rotors can also act as standards by which scanning probe chirality can be measured and assigned. Such atomic-scale geometric data about the STM tip allows unambiguous chirality assignment on individual, isolated, molecule basis for the first time.

Palladium and its alloys play a central role in a wide variety of industrially important applications such as hydrogen reactions, separations, storage devices, and fuel cell components. The exact mechanisms by which many of these processes operate have yet to be discovered. LT-STM has been used to investigate the atomic-scale structure of Pd/Au and Pd/Cu bimetallics created by depositing Pd on both Au(111) and Cu(111) at a variety of surface temperatures. We demonstrate that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H₂ flux on a Pd/Au sample with identical atomic composition and geometry.

4:00pm SS2-WeA7 Molecular Motion in Confinement, Z. Cheng, M. Luo, D. Sun, L. Bartels, University of California at Riverside
CO diffusion within a honeycomb network of anthraquinone molecules on a Cu(111) will be presented. The motion of the molecules is strongly affected by the confinement provided by the network. We observe the formation of a shell structure within pores, diffusion rates that strongly depend on the

coverage and imperfections of the coverage (e.g. dislocation lines) that appear thermodynamically stable.

4:20pm SS2-WeA8 Spatial Images of Different Vibronic Peaks at Single Molecule Level, Q. Huan, University of California, Irvine and Chinese Academy of Sciences, H.J. Gao, Chinese Academy of Sciences, W. Ho, University of California, Irvine

Spatial distributions of different vibronic peaks on single naphthalocyanine molecules adsorbed on an ultrathin aluminum oxide film are imaged by a scanning tunneling microscope in real space at low temperature. The spatial variations of electron-vibronic coupling in these images reveal the interplay between the molecular conformation, the vibrational modes and the molecular orbital structure, which are in accordance with spectra recorded at different locations over the molecule.

This work shows that vibronic imaging can provide rich information of electron-vibrational coupling at the single molecule level.

4:40pm SS2-WeA9 Stepwise Control and Spectroscopic Manifestation of the Target-Selective Single Bond Dissociation and Formation, Y.J. Jiang, W. Ho, University of California, Irvine

We demonstrated here, adopting a thiol-based π -conjugated molecule (1,4-bis[4'-(acetylthio)styryl]benzene), the evolution of the molecular electronic structure with the stepwise abstraction of different functional groups and the attachment of single gold atoms to sulfur anchoring atoms by scanning tunneling microscope (STM). The electronic resonances of the resultants were measured by spatially resolved electronic spectroscopy at each reaction step. It was revealed that the target-selective bond dissociations were initiated by electron populations of the spatially localized and energetically separated electronic resonances. Combining the well-controlled single bond scission with the lateral manipulation by STM tip, the details of Au-S bond formation and the influence of Au-S interaction on the electronic structure of the molecular junction were investigated in the well-defined contact geometry.

5:00pm SS2-WeA10 Surface Dynamics of Molecules in Single Internal (Vibrational and Rotational) States, V.L. Campbell, N. Chen, A.L. Utz, Tufts University

Beam-surface scattering studies of molecules prepared in a single internal quantum state provide a high level of control over the energetics and internal motion of the gas-phase reagent. Varying the identity of the laser-excited state permits a systematic survey of how vibrational excitation in the gas-phase reagent (bending or stretching excitation) impacts reactivity and reveals that both vibrational mode-selective and bond-selective chemistry is possible in a gas-surface reaction. Recently, we have begun to exploit the energetic control this approach offers to probe the dynamics of other energetic degrees of freedom. For example, state resolved reactivity measurements (S_0 vs. E_{trans}) of CH₄ dissociation on Ni(111) show that the shape of the sticking curve changes as a function of surface temperature. This change likely results from the modulation of the effective barrier to reaction along the translational energy coordinate as a function of surface atom position. Our experimental results are consistent with recent theoretical studies that point to an important role for surface atom motion in promoting dissociative chemisorption on Ni and Pt surfaces. The presentation will focus on our use of state-selected reagents to probe dynamics associated with other energetic degrees of freedom, such as surface atom motion. It will also describe advances in our experimental methods for acquiring these state-resolved data. These advances are transforming our ability to perform state-resolved measurements and will enable our extension of these methods to a much wider array of chemical systems.

5:20pm SS2-WeA11 3-Dimensional Velocity Map Imaging from Surfaces: A New Technique for the Study of Photodesorption Dynamics, S.P. Koehler, Y. Ji, University of California, Santa Barbara, D.J. Auerbach, GRT Inc., A.M. Wodtke, University of California, Santa Barbara

The ion imaging technique and the improved velocity map imaging (VMI) technique [1] have been successfully applied to many gas-phase photodissociation and crossed-beam experiments over the last 20 years [2]. The VMI technique maps two dimensional product velocity distributions to an image on a position sensitive detector and thus allows the measurement of product flux as a function of velocity for all velocities simultaneously.

Experiments on photo-desorption from surfaces have so far not used this elegant technique. Such experiments have often relied on time-of-flight (TOF) techniques to gain dynamical information about the process under investigation [3].

Here we show how Time-of-Flight (TOF) measurements can be coupled to the VMI technique to yield 3-dimensional velocity distributions for desorption products of surface photochemistry. In one example, we applied

this Three-Dimensional Surface Velocity Map Imaging (TDS-VMI) method to measure 193 nm photo-desorption of Br atoms from a KBr surface. Although this system has been studied in the past, the TDS-VMI technique reveals new features of the desorption dynamics. The velocity distributions indicate that at least two non-thermal mechanisms contribute to the photo-desorption dynamics. The TDS-VMI method also allows us to measure the yield of $\text{Br}(^2P_{3/2})$ and $\text{Br}(^2P_{1/2})$ over the full range of velocities that contribute to the photo-desorption process. The branching ratio $\text{Br}(^2P_{3/2})/\text{Br}(^2P_{1/2})$ is 24/1, a value that is quite different from that obtained previously.

Other examples will be discussed at the conference.

5:40pm **SS2-WeA12 Activated Quantum Diffusion of Hydrogen on Platinum(111)**, *A.P. Jardine, E. Lee, G. Alexandrowicz, H.J. Hedgeland, W. Allison, J. Ellis*, University of Cambridge, UK

Hydrogen atoms are one of the few surface species that are of sufficiently low mass for quantum processes to dominate surface transport. Here, we present the first quasi-elastic helium atomscattering (QHAS) measurements that demonstrate clear quantum effects in adsorbate diffusion. We use helium-3 spin-echo to make dynamic equilibrium measurements of the motion of H and D atoms on a Pt(111) surface, enabling lower temperatures to be studied than were possible with QHAS[1]. Our data shows a broken Arrhenius dependence, indicating two transport regimes; high temperatures (>120 K) and low temperatures (<110K). Otherwise, the data shows good agreement with a single jump model.

Our results offer a comprehensive dataset that is a severe test of theory. We compare the experimental data to existing protonic band structure calculations[2]. For H, it is possible to relate the measured activation energies to transitions to specific excited states of H, suggesting the diffusion of H on Pt(111) proceeds by activated quantum tunnelling. For D, the correspondence is less clear. We see a large change in pre-exponential factors with temperature, but not isotope, which we relate to energy exchange between adatoms and the surface. We compare the apparent rates of hopping with the expected tunnelling and energy transfer rates, in order to identify the rate limiting processes.

Recent work suggests that surface steps determine the macroscopic behaviour. However, our measurements are sensitive to the local, microscopic behaviour and give an alternative picture of the quantum motion[3].

[1] A. P. Graham, A. Menzel and J. P. Toennies, *J. Chem. Phys.* 111, 1676 (1999).

[2] S. C. Badescu, P. Salo, T. Ala-Nissila, S. C. Ying, K. Jacobi, Y. Wang, K. Bedurftig and G.Ertl, *Phys. Rev. Lett.* 88, 136101 (2002).

[3] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and Xudong Xiao. *Phys. Rev. Lett.* 97, 166101 (2006).

Thursday Morning, November 12, 2009

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference Room: C4 - Session IS+SS-ThM

In-Situ Spectroscopy - Interfacial Science & Catalysis Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-ThM1 Reduction of Cationic Sn in SnO_x/PtSn Alloy Surfaces**, *G. Liu*, Lehigh University, *H. Bluhm*, Lawrence Berkeley National Laboratory, *B. Koel*, Lehigh University

Understanding mechanisms of catalyst selectivity requires improved knowledge of oxidation and reduction reactions that occur at the metal/metal oxide interface. We describe studies that probe the thermal stability and reducibility of cationic Sn at SnO_x/PtSn alloy interfaces for several different and well-defined surface phases of SnO_x that can be formed depending on the temperature. Our investigations covered a wide range of conditions, from vacuum to the chemical changes during exposures to H₂ at pressures up to 5 Torr by using in-situ high pressure photoelectron spectroscopy (HP-PES). We find enormous differences in the reducibility of cationic Sn species showing that local surface structure and composition plays an key role in governing these reactions. These studies help to define the overall chemical reactivity of SnO_x species at these interfaces, and in particular, clarify the role of reduced and cationic Sn sites in selective hydrogenation of crotonaldehyde.

8:20am **IS+SS-ThM2 In-situ Study of the Oxidation of Pt(110)**, *M. Grass*, *D. Butcher*, *F. Aksoy*, *H. Bluhm*, *G.A. Somorjai*, *Z. Hussein*, Lawrence Berkeley National Laboratory, *B.S. Mun*, Hanyang University, Korea, *Z. Liu*, Lawrence Berkeley National Laboratory

The formation of oxides on transition metal surfaces has been actively studied because of its importance in understanding heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxides on Pt(110) has received much attention. Oxidation reactions over Pt are both industrially significant and fundamentally intriguing. In particular, there has recently been much debate over the surface structure and reaction mechanism of CO oxidation at high O₂/CO ratios on Pt(110).

In this study, we used both ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and high pressure scanning tunneling microscopy (HP-STM) to investigate oxidation of Pt(110) as a function of O₂ pressure, temperature and gas composition (CO, O₂). AP-XPS results demonstrate that two different surface oxygen species form on Pt(110) surface above 500 mTorr O₂: chemisorbed oxygen and an island structured species that extends at least two Pt layers deep. HP-STM images under the same conditions confirm the formation of these oxide islands. We present here the pressure and temperature dependence of both oxygen species as well as kinetic measurements of the reaction CO_{ad} + O_{ad} → CO₂ for each of the adsorbed oxygen species.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Light Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

8:40am **IS+SS-ThM3 Composition and Chemistry of the Liquid/Vapor Interface by In-Situ X-ray Photoelectron Spectroscopy**, *J.C. Hemminger*, University of California, Irvine **INVITED**

We use synchrotron based x-ray photoelectron spectroscopy (XPS) experiments to study the composition and chemistry at the liquid/vapor interface of aqueous solutions. These experiments are motivated by an interest in the fundamental behavior of aqueous interfaces as well as applications to aqueous aerosols in the atmosphere. We take advantage of the variable energy characteristic of synchrotron radiation to carry out XPS experiments as a function of experimental probing depth, thereby generating a depth profile of the liquid/vapor interface. Recent experiments in which we have studied the composition of aqueous salt solutions in the presence of organic surfactants will be described. In addition, studies of acid/base equilibria at the liquid/vapor interface will be described. Our depth profile experiments show that the acid/base equilibrium at the solution surface is modified by the differences in bulk solubility of the acid and base involved in the equilibrium. Two different experimental approaches have been used: an ambient pressure end station at the Advanced light source is equipped with a differentially pumped electron

energy analyzer allowing studies with the sample chamber at pressures of a few torr. This system has been used to study saturated aqueous solutions of alkali halide salts. A liquid/jet endstation at the BESSY synchrotron has allowed us to study the surface segregation of molecular ions such as nitrate in aqueous solutions as a function of solution concentrations.

9:20am **IS+SS-ThM5 Oxidation Studies of Gold by in Situ High-Pressure X-ray Photoelectron Spectroscopy**, *F. Borondics*, *P. Jiang*, Lawrence Berkeley National Laboratory, *S. Porsgaard*, Lawrence Berkeley National Laboratory & iNANO University of Aarhus, Denmark, *M. Köber*, *A. Caballero*, *H. Bluhm*, *M. Salmeron*, Lawrence Berkeley National Laboratory

The high catalytic activity of nanometer size gold particles in various chemical reactions has been intensively investigated in the recent years. However the origin of the exceptional catalytic properties of Au is still strongly debated in many cases ranging from the mobilization of gold under catalytic conditions through the oxidation state of the active Au species during the reaction.

In this study we focus on the interaction of oxygen with Au that has been proposed to play an important role in the mechanism of oxidation reactions. Using in situ high-pressure X-ray photoelectron spectroscopy (HP-XPS) and in situ scanning electron microscopy we studied the different model systems, such as bulk gold, evaporated sub-monolayer and different size nanoparticle samples using single crystalline TiO₂ (110) as substrate.

Our results show that gold oxidation can be induced under certain conditions, such as high intensity X-rays or reactive ozone atmosphere. The existence of gold oxide has been mentioned in the literature, but our systematic studies provide a better understanding of the formation and stability of this compound, which is not only a chemical curiosity being the oxide of the noblest metal, but can be very important in designing more efficient catalysts. In addition, we would like to draw the attention of the community to a number of artifacts that can easily lead to misinterpretation of experimental data.

The implications of our results should be considered in the field of catalysis, nano- and surface science as well as in situ high-energy spectroscopies.

9:40am **IS+SS-ThM6 Anchoring of N3 Dye Molecule on TiO₂(110) Surface and its Influence on Energy Level Alignments**, *P. Nachimuthu*, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *Z. Zhu*, *K.M. Beck*, *S. Thevuthasan*, *M.A. Henderson*, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the electronic coupling between the dye-sensitizer and TiO₂ determines the alignment of energy levels and the electron transfer dynamics. This electronic coupling is strongly modified by the way in which the dye molecules are adsorbed and anchored to TiO₂ surface, its relative orientations and geometrical structures. The present study is an attempt to understand how the dye molecules are bound to TiO₂ single crystal surface and their influence on the energy level alignments and electron transfer dynamics. Controlled adsorption of dye molecules (bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II) is known as N3) onto TiO₂ surface has been carried out to obtain desired anchoring and orientations by varying the concentration, hydrophobic substituents on dye and defect concentrations (in TiO₂). ToF-SIMS and PEEM mapping techniques were used to understand the distribution of dye molecules on TiO₂ surface. The XPS and UPS measurements were carried out to determine the structural and electronic properties including the stoichiometry of dye molecules on TiO₂ surface, the relative energy levels and band offsets in the absence and presence of UV light. The XPS results show that the atomic ratios of S to Ru and N to S are ~1 and ~5, respectively, which correspond to a non-stoichiometric composition of N3 molecule on TiO₂ surface. The theoretical atomic ratios of S to Ru and N to S in N3 molecules are 2 and 3, respectively. This suggests that an isothiocyanide group from N3 molecule is lost from the surface of TiO₂. The XPS from multilayers of N3 molecules on Si surface however show stoichiometric composition.

10:40am **IS+SS-ThM9 Scanning Transmission X-ray Microscopy of Inorganic and Organic Nanoparticles in the Environment**, *S.C.B. Myneni*, Princeton University **INVITED**

Inorganic and organic nanoparticles are common in the environment, and play an important role in the biogeochemical reactions occurring in the natural systems. However, their chemistry and behavior are poorly understood. Using STXM, researchers can examine the chemistry and mineralogy of these particles, and the functional group chemistry of associated organic molecules. While XANES spectral features are used routinely to identify the oxidation states of elements in minerals

successfully, fine variations in spectral features of minerals can be used in the identification of minerals and the crystallinity of precipitates/nanoparticles. The XANES spectra are also sensitive to different functional groups and their protonation (or deprotonation) and metal complexation; unique features in XANES spectra can also be used in mapping the distribution and relative concentrations of organic molecules and their complexes at a resolution better than 25 nm in environmental samples. In the last 4-5 years, we made significant progress in the understanding of the mineralogy and chemistry of important environmental nanoparticles and biominerals because of the development of STXM capabilities. A summary of applications of STXM in studying environmental nanoparticles, and highlights of some of these recent findings will be discussed.

11:20am **IS+SS-ThM11 In-situ Characterization of Arsenic on Model Iron Oxide Surfaces**, *S. Kaya, F. Mbuga*, SLAC National Accelerator Lab, *T. Kendelewicz*, Stanford University, *J. Newberg, H. Bluhm*, Lawrence Berkeley National Lab, *H. Ogasawara*, SLAC National Accelerator Lab, *G.E. Brown*, Stanford University, *A. Nilsson*, SLAC National Accelerator Lab

Natural contamination of groundwater by arsenic has become an important water quality problem in many parts of the world [1]. Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. Iron oxides play a significant role in controlling dissolved As concentration and limit the mobility and availability of As(III) and As(V). Arsenic adsorption mechanisms involve exchange of the As species for surface water and surface OH groups therefore in-situ characterizations of iron oxide surfaces in the presence of water are crucial.

We have studied chemical nature of As on Fe₃O₄(111) and Fe₃O₄(111)/Fe(OH)_x thin films in the presence of water (P<0.5 Torr) using Ambient Pressure Photoemission Spectroscopy (APPEs) at Advanced Light Source (ALS) [2]. Hydroxylation of pristine Fe₃O₄(111) surface commences at low relative humidity (RH) values and is followed by adsorption of molecular water with increasing RH. In 0.5 Torr water H₂O:OH ratio at room temperature is about one and all acidic sites are fully hydroxylated. As 3d spectra taken in presence of 0.5 Torr water suggests that oxidation state of arsenic depends on degree of hydroxylation of iron oxide surfaces studied. In addition to the hydroxylation process, increasing RH leads to oxidation of arsenic from As(III) to As (V). Fe²⁺ surface sites plays an important role in the oxidation states of arsenic and the reasons of which will be discussed based on the changes in formal charges during hydration-dehydration processes.

[1] R. Nickson, et. al., Nature, 395 338 (1998).

[2] H. Bluhm et al., MRS Bulletin, 34 1022 (2007).

11:40am **IS+SS-ThM12 Kinetic Studies of the Dissociation of Molecular Oxygen on Pt(111)**, *H. Ogasawara, L.-Å. Näslund, D.J. Miller, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

Thermally programmed X-ray photoelectron spectroscopy was used to study the dissociation of molecular oxygen on Pt(111) under ultrahigh vacuum conditions. Sub-monolayer coverages of molecular oxygen were dosed onto a clean crystal of Pt(111) at 60 K, a temperature well below the dissociation onset of roughly 95 K. Kinetic analysis of the XPS data indicate that they are consistent with a barrier to O₂ dissociation that is less than 0.4 eV. This result is in striking contrast to the most recent theoretical studies with density functional theory, which all indicate barriers in excess of 0.5 eV (0.5 - 0.9 eV). On the basis of this low observed barrier, we speculate that the direct dissociation of molecular oxygen could be a viable alternative to the associative and peroxide pathways that are presently assumed to be operative in the oxygen reduction reaction.

Surface Science

Room: M - Session SS1+AS+TF-ThM

Surface Science of Hazardous Materials

Moderator: V. Grassian, University of Iowa

8:00am **SS1+AS+TF-ThM1 Interactions of Nerve Agents with Model Surfaces: Computational Approach**, *J.R. Leszczynski*, Jackson State University **INVITED**

The talk summarizes the results of recent studies performed by our group. They include modeling of interactions of selected nerve agents with model surfaces. Among studies nerve agents are soman, sarin, tabun and their surrogates. We investigated different types of surfaces: metals, metal oxides and clays. The study was performed using various techniques of non-

empirical, ab initio methods. Among predicted characteristics are molecular geometries of resulting complexes, their interaction energies, electrostatic potentials, and IR spectra. We identified the most promised surfaces that facilitate decomposition of the selected nerve agents. Also, predicted differences between selected processes for nerve agents and their simulants will be discussed.

8:40am **SS1+AS+TF-ThM3 Ab-Initio Computational Approaches to the Adsorption of Chemical Warfare Agents**, *V. Bermudez*, Naval Research Laboratory

Computational chemistry can be used to great advantage in dealing with chemical warfare agents (CWAs). Computation can be applied to reagents which are much too dangerous for routine experimentation as well as to non-traditional species which have not yet been (but could be) synthesized. Examples will be given from recent work¹ on the interaction of the simulant dimethyl methyphosphonate (DMMP) and the real CWAs Sarin and VX with γ -Al₂O₃ surfaces. The γ -Al₂O₃ surface acts as a Lewis acid (electron acceptor) when OH-free and a Brønsted acid (proton donor) when hydroxylated. Thus γ -Al₂O₃ is an excellent prototype for a wide range of other metal oxides. DMMP, Sarin and VX all adsorb in the same way and with a similar adsorption energy (ΔE_{ads}) which depends strongly on surface acidity. A coordinatively-unsaturated tetrahedral Al(*T_d*) site, which is a strong Lewis acid, forms an Al---O=P dative bond to the phosphonyl group. This is always the most favorable site, and an agent adsorbed by hydrogen bonding at an OH site will migrate to a bare Al(*T_d*) site if one is available. The γ -Al₂O₃ lowest unoccupied orbital is a surface state associated with the Al(*T_d*) site which lies just below the conduction band minimum. The energy of this state relative to vacuum is a quantitative measure of Lewis acidity and is directly reflected in ΔE_{ads} . The highest occupied orbital of the molecule is a non-bonding orbital on the phosphonyl O atom. The one-electron energy of this orbital also directly affects ΔE_{ads} . The hydroxylated surface forms Type I, II and III OH sites with O bonded to one, two or three Al's respectively. Brønsted acidity, and ΔE_{ads} for OH---O=P bond formation, increase in the order I<II<III with the Type I interaction being almost negligible. The amine group in VX is found to be a strong base, capable of deprotonating an acidic Type III OH site to form an ammonium ion even in the absence of a polar solvent. The electronic excitations of DMMP, Sarin and VX have also been investigated with the goal of identifying possible photochemical effects due to terrestrial solar radiation (TSR). This issue has been largely overlooked in previous agent-fate studies. DMMP and Sarin are insensitive at energies below ~7 eV; however, vapor-phase VX can be excited near 4.3 eV which is at the upper end of the TSR. The excitation threshold changes slightly for adsorbed VX, shifting to the red or to the blue depending on the nature of the surface. These results provide a predictive framework for understanding the effects of surface condition on the adsorption of VX and G-series CWAs on oxide surfaces.

(1) Supported by the Defense Threat Reduction Agency (DTRA)

9:00am **SS1+AS+TF-ThM4 Computational Prediction of Physical Properties and Environmental Reactivity of Nitro-aromatic and Hydrogen Reach Explosives**, *L.G. Gorb, F.C. Hill*, SpecPro, Inc., *E.N. Muratov, A.G. Artemenko, A.V. Bogatsky* Physical-Chemical Institute, Ukraine, *Y.I. Kholod*, Jackson State University, *V.E. Kuz'min, A.V. Bogatsky* Physical-Chemical Institute, Ukraine, *J.R. Leszczynski*, Jackson State University

Prediction of chemical and physical properties of explosives and products of their environmental degradation, instead of expensive and toxic chemical experiments, is a very important task from many points of view. Among them water solubility (SW) is an extremely important property of chemical compounds. It plays a major role in definition of migration and ultimate fate of chemicals in the environment. In particular, high solubility leads to expeditious distribution in water, i.e., chemicals that rapidly and completely dissolve in water will be transported along with the general flow of water. High SW is generally associated with a very low affinity for adsorption to solids in water, e.g., soil particles or sediment. In addition, high water solubility is associated with accumulation of contaminants in living organisms.

Water solubility values for twenty seven nitro-aromatic and hydrogen reach compounds with experimentally measured values were computed using the conductor-like screening model for real solvent (COSMO-RS) based on the density functional theory and COSMO technique. We have found that the accuracy of the COSMO-RS approach for prediction of water solubility of liquid nitro compounds is impressively high (the errors are lower than 0.1 LU). However, for some solid nitro compounds, especially nitramines, there is sufficient disagreement between calculated and experimental values. In order to increase the accuracy of predictions the quantitative structure-property relationship (QSPR) part of the COSMO-RS approach has been

modified. The solubility values calculated by the modified COSMO-RS method have shown much better agreement with the experimental values (the mean absolute errors are lower than 0.5 LU). Furthermore, this technique has been used for prediction of water solubility for an expanded set of twenty three nitro compounds including nitroaromatic, nitramines, nitroanisoles, nitrogen rich compounds and some their nitroso and amino derivatives with unknown experimental values.

Finally, an application of COSMO-RS approximation to the prediction of environmental reactivity for hydrogen reach explosives (alkali hydrolysis in water) has been briefly discussed

9:20am **SS1+AS+TF-ThM5 A Material Approach to Enable Detection of Toxic Chemicals in Water by IR Spectroscopy**, *C.P. Tripp*, University of Maine **INVITED**

We are currently developing a detection system based on the principles of infrared (IR) spectroscopy that operates in heterogeneous aqueous environments and provides fast detection (< 10 min) and high sensitivity to chemical warfare agents and other toxic chemicals with minimal false alarms. The key enablers to using infrared spectroscopy for aqueous based detection are the development of materials that lead to selective and robust sampling protocols. In this talk, I will present new sampling methods that are based on the use of surface functionalized adsorbents and reactive thin films coated onto a porous and IR amenable support. The coatings chemically react with a predefined class of compounds and identification of the specific chemical is provided by IR spectral analysis. Examples of this approach for low level detection of cyanide, metals, pesticides, and chemical warfare agents in water will be demonstrated.

10:40am **SS1+AS+TF-ThM9 Surface Science and its Application to Energetic Materials**, *V.J. Bellitto, J.M. Kelley, D.N. Sorensen*, Naval Surface Warfare Center

Composite explosives and propellants are heterogeneous admixtures of crystalline powders in a rubbery binder. Materials such as aluminum are added to enhance specific performance criteria. The aluminum although improving performance in systems may not be efficiently consumed. Placement of explosives and propellants in closer proximity with the metal is expected to provide performance enhancements. The novel material should have more complete combustion and faster energy release rates as problems with heat transfer and diffusion rates are overcome.

We have undertaken a research effort to gain a fundamental understanding of the metal/explosive interaction. In performing experiments novel interfaces are produced which are not obtainable under ambient conditions. The research reveals possible avenues for the development of new energetic materials with improved performance.

In this work, X-ray photoelectron spectroscopy (XPS) was used to study the interaction of aluminum with cyclotrimethylenetrinitramine (RDX) and the resultant products analyzed via Differential Scanning Calorimetry (DSC). For RDX, the spectrum of the N 1s region has two easily discernable peaks assigned to the nitro group and ring structure nitrogen. Upon the initial interaction of aluminum with RDX, the N 1s spectrum reveals that the nitrogen peak associated with the nitro group is diminished compared to that of the ring structure. This is an indication of the preferential reaction of the nitro group with the aluminum, leaving the ring structure intact. The data also shows the preferential formation of aluminum oxide species over aluminum nitride species. Continued deposition of aluminum produces aluminum layers over the initial oxide layer. The DSC data demonstrates an increase in decomposition energy through the placement of metal directly onto the explosive surface.

11:00am **SS1+AS+TF-ThM10 Characteristics and Stability of Oxide Films on Plutonium Surfaces**, *H.G. García Flores*, University of Nebraska-Lincoln and Los Alamos National Laboratory, *A.L. Broach, D.P. Moore*, Los Alamos National Laboratory, *D.L. Pugmire*, Los Alamos National Laboratory and University of Nebraska-Lincoln

The oxidation of plutonium metal continues to be an area of considerable activity. The reaction characteristics have significant implications for production use, storage, and disposition of this reactive material. Developing an accurate physical model of the structures, oxidation states, and oxygen concentration gradients present during oxidation are essential to understanding this process. Traditionally, the stable oxides of plutonium have been thought to be plutonium sesquioxide (Pu_2O_3 , O/Pu=1.5, Pu^{3+}) and plutonium dioxide (PuO_2 , O/Pu=2.0, Pu^{4+}), existing in a layered structure on oxidized plutonium metal. Many studies of this system are performed under ultra-high vacuum (UHV) using surface sensitive techniques to probe oxidation states, electronic structure, and surface chemistry.

Here, we report on a detailed study using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to measure the relative concentrations of oxygen and plutonium, as well as the resulting oxidation

states in the near-surface region. It has previously been shown that under UHV conditions, PuO_2 undergoes an auto-reduction reaction to the more stable Pu_2O_3 . The auto-reduction of PuO_2 occurs as oxygen diffuses from the surface, through the oxide-film, to the metal-oxide interface.¹ The results of this study show a much greater than anticipated extent of auto-reduction and challenge the commonly held notion of the stoichiometric stability of Pu_2O_3 thin-films, especially in the presence of plutonium metal. The data indicates that a hypo-stoichiometric plutonium oxide ($\text{Pu}_2\text{O}_{3-y}$) exists at the metal-oxide interface. A new model of the plutonium/oxygen thin-film system will be proposed and its applicability to thicker-films will be discussed.

¹ Morrall P, Tull S, Glascott J, Roussel P, 2007 *J.Alloys Comp.* **444-445** 352.

Surface Science

Room: N - Session SS2-ThM

Electron Activated Molecular Interfaces

Moderator: S.L. Tait, Indiana University

8:00am **SS2-ThM1 Thermal Effects of Templated C₆₀ Ordered Structures on AnCA**, *B. Xu*, Yanshan University, China

Anthracene carboxylic acid (AnCA) forms multiphase self-assembly structures on Ag(111). Two of these multiphase structures were employed to investigate the template effects on sequentially deposited C_{60} molecules using scanning tunneling microscopy. At low C_{60} coverage, fullerene molecules tend to occupy Ag step edge or AnCA domain boundary sites. With increasing C_{60} deposition, strong modulation on C_{60} growth was observed depending on the initially AnCA structures. C_{60} can either pair into dimers and locate on top of AnCA molecules with the periodicity determined by the underneath AnCA (Interface I), or form small phase-separated C_{60} and AnCA domains with the width of tens of nanometers (Interface II). Anneal these interfaces at 370 K lead to the desorption of most of the AnCA molecules and the formation of novel C_{60} structures. For Interface I, the second layer C_{60} molecules are organized into ordered dimers on top of the first layer zigzag C_{60} chains running along Ag[1-10] direction. The distance between neighboring zigzag C_{60} chains is 2 nm, and there are some AnCA molecules left between the zigzag chains to hold the structure stable. For Interface II, parallel C_{60} chains along Ag[11-2] are observed after annealing. The C_{60} molecules are close packed along the chain direction and separated by *c.a.* 1.3 nm between neighboring chains. The molecules have alternative heights across the chain direction, suggesting distinct molecular orientations. Our studies suggest a pathway of nanostructure fabrication through the choice of suitable template and annealing treatment.

8:20am **SS2-ThM2 Porphyrin Adsorption on Copper Single Crystal Electrodes Studied by SXPS**, *S. Breuer, D.-T. Pham*, University of Bonn, Germany, *G. Cherkashinin, T. Meyer*, Technical University of Darmstadt, Germany, *P. Broekmann*, University of Berne, Switzerland, *K. Wandelt*, University of Bonn, Germany

Porphyrins are well known as biologically active molecules, e.g. as heme in hemoglobin or chlorophyll in green leaves. Their biological functions originate from their redox activity, which makes their investigation in an electrochemical environment interesting. We have investigated the electrochemically deposited monolayers of Tetra-methylpyridinium-porphyrin (TMPyP)-Tetratosylat on chloride and sulphate precovered Cu(100) and Cu(111) surfaces by means of Cyclic Voltammetry (CV), in-situ Electrochemical Scanning Tunneling Microscopy (EC-STM) as well as ex-situ X-ray Photoelectron Spectroscopy with synchrotron radiation S-XPS at the SoLiAS-station at BESSY II. This station allows the electrochemical preparation of the surfaces and a quick and contaminationfree transfer into UHV. The electrochemical preparation includes the formation of the anion preadsorption in diluted hydrochloric- or sulphuric-acid, respectively, and the adsorption and emersion of the porphyrin layer at different potentials within the doublelayer regime.

While the preadsorbed anion layers, i.e. $\text{c}(2 \times 2) \text{Cl}^-$ on Cu(100), $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Cl}^-$ on Cu(111), quasi- $(\sqrt{3} \times \sqrt{7})\text{R}30^\circ\text{-SO}_4^{2-}$ on Cu(111) and a disordered SO_4^{2-} -layer on Cu(100), bind the TMPyP-cations electrostatically to the surface variation of the electrode potential causes structural transitions within the selfassembled porphyrin layers, as seen with EC-STM. The S-XPS N(1s) spectra enable a clear correlation of the structural changes with concomitant redox-transition of the TMPyP-cations. As a result structural transitions within the ordered TMPyP-layers are most likely

due to different lateral electrostatic interactions between different TMPyP-redox states.

8:40am SS2-ThM3 STM and XPS Study on the Reactive versus Non-Reactive Adsorption of Viologens, D.-T. Pham, C. Safarowsky, S. Huemann, S. Breuer, University of Bonn, Germany, R. Hunger, Technical University of Darmstadt, Germany, P. Broekmann, University of Berne, Switzerland, K. Wandelt, University of Bonn, Germany

The reactive and non-reactive adsorption of redox-active viologens (1,1'-disubstituted-4,4'-bipyridinium molecules) on a chloride modified copper electrode has been studied using a combination of cyclic voltammetry (CV), in-situ scanning tunneling microscopy (STM) and ex-situ photoemission techniques. Two prototypes of viologens, 1,1'-dibenzyl-4,4'-bipyridinium molecules and 1,1'-diphenyl-4,4'-bipyridinium molecules (abbreviated as DBV and DPV respectively), are studied here with respect to their redox behaviour upon adsorption on a chloride modified copper surface. DBV molecules can be adsorbed and stabilized on a chloride modified Cu(100) electrode surface in their di-cationic state at potentials above the main reduction wave in the cyclic voltammogram. Electrostatic attraction between the solvated viologen di-cations and the anionic chloride layer is the main driving force for the DBV adsorption onto the electrode surface. By reducing the adsorbed dicationic DBV²⁺ species to the corresponding radical mono-cation DBV^{•+}, a quasi-reversible phase transition is initiated from a "cavitand" to a "stripe pattern" phase on the chloride layer. Analysis of the N1s and O1s core level shifts of the adsorbed DBV molecules points to a non-reactive DBV adsorption leaving the DBV²⁺_{ads} solvation shell partly intact. The laterally ordered DBV²⁺_{ads} monolayer is highly hydrophilic with at least 8 water molecules per viologen present within this cationic organic film. The analysis of the Cl2p core level shift reveals that no other chloride species is present on the surface than the one underneath the organic molecules in direct contact with the metallic copper surface.

DPV²⁺ molecules are much more reactive upon adsorption and cannot be stabilized on the electrode surface in di-cationic state, at least within the narrow potential window of copper. The N1s core level shift points to DPV²⁺ molecules which are upon adsorption instantaneously reduced to the corresponding mono-reduced DBV^{•+}_{ads} species even at potentials above the main redox wave in the voltammogram. This process leads to the formation of a highly hydrophobic monolayer film with polymeric DBV^{•+}_{ads} stacking chains as the characteristic structural motif.

9:00am SS2-ThM4 Interfacing Electrocatalytic Molecules with Vertically Aligned Carbon Nanofibers through Click Chemistry: An Approach to "Smart", Highly Functional Nanostructures, E.C. Landis, R.J. Hamers, University of Wisconsin, Madison

Vertically Aligned Carbon Nanofibers are a unique form of nanoscale carbon comprised of graphene cups nested together to form a nanofiber. A unique feature of VACNFs is that they expose large amounts of graphene edge-planes along the nanofiber sidewalls. The high electron transfer rates associated with edge plane graphite suggest that VACNFs should be an excellent support for electrocatalysis. However, nanofibers alone lack the specificity often desired in electrochemical reactions. We have developed a method for covalently binding redox active molecules to the VACNF surface based on "click" chemistry as a pathway toward combining the high stability of VACNFs with the selectivity provided by molecular redox-active groups. This binding method creates a highly stable linkage of VACNFs to a 'smart' ligand with well defined redox properties. Using XPS, FTIR, and other surface analytical methods in conjunction with electrochemical measurements, we have investigated how the nanoscale structure of the fibers and the nature of the surface ligands impacts the surface chemistry and subsequent electron transfer processes. Our results demonstrate that the graphitic edge-plane sites of VACNFs play a key role in the chemical reactivity of VACNFs and in the subsequent electron-transfer processes on VACNFs functionalized with redox-active groups. These results demonstrate that VACNFs are a promising material for functional nanostructures using covalently tethered molecular catalysts.

9:20am SS2-ThM5 Fabrication of a Full-Coverage Polymer Nanobrush on Electron-Beam-Activated Monomolecular Template, S. Schüp, N. Ballav, M. Zharnikov, University of Heidelberg, Germany

Along with chemistry, morphology is an important tool to adjust properties of surfaces and interfaces. One of the most promising approaches to control over surface morphology down to the nanometer scale is the fabrication of 3D polymer brush patterns by surface-initiated polymerization (SIP) combined with electron beam lithography (EBL). However, polymer brush patterns made by EBL-SIP are chemically inhomogeneous. Whereas the polymer brush itself is comprised of a polymer, the areas between the 3D features have a different chemical identity determined by the original template. As a result, the effects of morphology on one side and chemistry and surface energy on the other side can be entangled when using such

patterns as model surfaces for, e.g., biology-inspired research. Here, we show that this drawback can be overcome by using a sophisticated primary template comprised of monomolecular film with mostly deactivated amino tail groups suitable for SIP. Whereas SIP on such a template gives a thin, homogeneous "background" brush, the regeneration of these groups by electron beam activation lithography promotes the controlled growth of 3D polymer features on this background, resulting in the formation of chemically homogeneous morphology pattern exclusively comprised of the polymer material. The technique relies upon commercially available compounds and requires a comparably low patterning dose. Using a biologically relevant polymer, poly-N-isopropylacrylamide, as a test system, we demonstrated the fabrication of both complex gradient-like brushes and marine-mammals-skin-inspired surfaces on the electron-beam-engineered monomolecular templates.

9:40am SS2-ThM6 Self-assembled Monolayers as Templates for Electrochemical Nanotechnology, C. Shen, University of St Andrews, UK, C. Silién, University of Limerick, Ireland, M. Buck, University of St Andrews, UK

Electrochemistry and self-assembled monolayers (SAMs) are a versatile combination as, on the one hand, SAMs can be used as templates to control electrochemical processes whereas electrochemistry, on the other hand, allows manipulation of SAMs [1,2].

Within this context underpotential deposition (UPD) of metal, i.e. intercalation of a metal monolayer at the SAM-substrate interface, is particularly interesting as this alters the electrochemical stability of a SAM. However, to exploit this for a controlled manipulation of SAMs on the nanoscale it is mandatory to use SAMs of very high quality in order to eliminate uncontrolled metal UPD caused by defects in a SAM [3]. In our experiments we use a class of thiol SAM whose molecules are characterized by the combination of a rigid aromatic moiety with an aliphatic spacer. Forming layers of high structural perfection defects are then introduced in a controlled way by

local modification of a SAM using, for example, the tip of a scanning tunneling microscope. By this means UPD of metal and subsequent modification of the SAM can be controlled on a length scale ranging from micrometers down to nanometers.

[1] Thom, I.; Hähner, G.; Buck, M. Appl. Phys. Lett. 87, 024101 (2005).

[2] Oyamatsu, D.; Nishizawa, M.; Kuwabata, S.; Yoneyama, H. Langmuir 14, 3298 (1998).

[3] Silién, C.; Buck, M. J. Phys. Chem. C 112, 3881 (2008).

10:40am SS2-ThM9 XPS and AFM Characterization of Two Component Self-Assembled Monolayers on Au(111), M.H. Cheng, T. McIntire, R.L. Grimm, J.C. Hemminger, University of California, Irvine

Water uptake on organic films is of great importance in a number of fields. We have used two-component alkanethiol self-assembled monolayers (SAMs) to prepare surfaces with varied hydrophilic character. These surfaces have been used to study water uptake as a function of hydrophilic/hydrophobic character. The chemical composition and morphology of the two two-component alkanethiol self-assembled monolayers on Au(111) were characterized by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Gold films on glass were prepared by piranha cleaning and *in vacuo* argon ion sputtering yielding carbon- and oxygen-free surfaces. Solution-phase chemistry forms a two-component SAM comprised of the octanethiol and 6-mercaptohexanoic acid. These components were selected for comparison with previous research in our laboratory regarding the interaction and temperature-programmed desorption (TPD) of water from organic surfaces of tuned hydrophobic and hydrophilic character. The ratio of the O(1s) to the Au(4f) peak areas in the XPS quantify the relative fraction of the carboxylic acid-terminated thiol in the SAM. The XPS spectra indicate that the relative fraction of the two thiol components in the surface adsorbed SAM phase does not correspond to the relative solution-phase concentrations. By comparison with water thermal desorption experiments, we discuss the implications for the interaction of water with methyl-terminated and carboxylic acid-terminated organic surfaces and partially-oxidized organic aerosol.

11:00am SS2-ThM10 Vacancy Diffusion in Self-Assembled Organic Monolayers and its Role as a Roughening Mechanism in Organic/Organic Interfaces, C. Urban, D. Eciya, M. Trelka, Universidad Autonoma de Madrid, Spain, R. Otero, UAM & IMDEA-Nano, Spain, J.M. Gallego, ICMC-CSIC, Spain, N. Martín, Universidad Complutense de Madrid, Spain, R. Miranda, UAM & IMDEA-Nano, Spain

Molecular diffusion on solid surfaces is of fundamental importance for surface chemistry and also because of the important role it plays in the formation of self-assembled molecular mono and multilayers. Many studies have discussed the diffusion processes of a single, isolated molecule on the

surface and the self-assembly process in terms of molecule-molecule and molecule-substrate interactions, but the relevant kinetic aspects have mostly not been dealt with. In addition, the growth of organic multilayers of two different types of functional molecules (e.g. donor and acceptor or magnetic and non-magnetic) with enough structural perfection requires a knowledge of intermixing processes at interfaces not yet available and intimately related to vacancy diffusion.

We directly visualized the surface diffusion of molecular vacancies in monolayers of exTTF (2-[9-(1,3-dithiol-

2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole) self-assembled on Au(111) under UHV conditions. exTTF is a strong electron donor, and in combination with PCBM, it has been shown to produce a phase-segregated, mixed layer with optimal morphology for bulk heterojunction solar cells [1]. When deposited on Au(111), exTTF molecules modify the substrate surface reconstruction and self-assemble to form long rectangular islands, the space between them being occupied by a sea of diffusing, non-nucleated molecules, which are very mobile even down to 150 K. The continuous exchange of molecules between the islands and this sea creates many vacancies within the islands. By means of a variable temperature fast-STM, we have quantified the diffusion of these vacancies within the islands. The results indicate a non-isotropic, Brownian-type diffusion. The implication of these results and the relevance of this diffusion mechanism for the exchange processes observed in the growth of exTTF-PCBM mixed layers and multilayers will be discussed.

[1] R. Otero, D. Écija, G. Fernández, J.M. Gallego, L. Sánchez, N. Martín, R. Miranda, *Nano Letters* 7 (2007) 2602-2607.

11:20am **SS2-ThM11 Local Fluctuations in Organic Adlayers - a Quantitative Video-STM Study**, *M. Roos, T. Waldmann, H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded networks on different substrates at solid surfaces.^{1,2} Using time resolved scanning tunneling microscopy we have studied selected dynamic phenomena in such adlayers on Au(111) and Ag(111) at around room temperature. Specifically, we have evaluated the mobility of defects in ordered adlayers, exchange of molecules between 2D phases of different local coverage and structure and fluctuations within disordered phases. Such data not only provide important information about typical rates in self assembly processes, but also give quantitative insights into molecular-scale aspects that govern the adlayer thermodynamics. Apart from the balance of molecule-molecule and molecule-substrate interactions, we find a surprisingly high influence of molecular entropy due to rotation and translation on the stability of the distinct phases. We will discuss the relevance of our findings for these particular model systems for the growth and stability of supramolecular structures in general.

¹ M. Roos et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5672.

² H. E. Hoster et al., *Langmuir* 23 (2007) 11570.

11:40am **SS2-ThM12 From Self-Assembled Monolayers to 1 nm Thin Conducting Carbon Nanosheets**, *A. Turchanin, A. Beyer, Ch.T. Nottbohm, X. Zhang*, University of Bielefeld, Germany, *R. Stosch*, PTB-Braunschweig, Germany, *A. Sologubenko, J. Mayer*, University of Aachen, Germany, *P. Hinze, T. Weimann*, PTB-Braunschweig, Germany, *A. Götzhäuser*, University of Bielefeld, Germany

Whereas the fabrication of free-standing 0D and 1D nanomaterials like clusters, nanoparticles, nanowires, nanotubes etc. is well established at present, the fabrication of free-standing 2D materials with atomic thicknesses is not routine. In this contribution we present a route for the fabrication of novel ultrathin (~1 nm) free-standing carbon nanosheets with adjustable sizes based on molecular self-assembly. Self-assembled monolayers (SAM) of aromatic biphenyl molecules are first cross-linked by electrons [1]. Vacuum pyrolysis of the cross-linked films transforms them into a mechanically stable and conductive 2D graphitic phase consisting of nanosize graphene patches [2, 3]. Resistivity and stiffness can be tuned by the annealing temperature [3]. The transition from insulator to conductor (~100 kΩ/sq) is characterized by a variety of complementary spectroscopic and microscopic techniques (Raman Spectroscopy, XPS, UPS, NEXAFS, TDS, HTEM, STM, AFM). A plethora of applications of this novel material is visible taking advantage of the fact that size, shape, and resistivity of the nanosheets in supported and suspended states (nanomembranes) are easily controlled.

[1] W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Götzhäuser, M. Grunze, *Appl. Phys. Lett.* 75, 2401 (1999)

[2] A. Turchanin, M. El-Desawy, A. Götzhäuser, *Appl. Phys. Lett.*, 90, 053102 (2007)

[3] A. Turchanin, A. Beyer, Ch. T. Nottbohm, X. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Götzhäuser, *Adv. Mater.* 21, 1233 (2009)

Thursday Afternoon, November 12, 2009

Surface Science

Room: M - Session SS1-ThA

Nucleation and Growth - Metals

Moderator: G.F. Verbeck, University of North Texas

2:20pm **SSI-ThA2 Influence of Quantum Well States on the Formation of Surface Au/Pb Alloy in Pb/Si(111) Quantum Thin Films.** J.D. Kim, S.Y. Qin, A. Khajetoorians, The University of Texas, Austin, W.G. Zhu, Z.Y. Zhang, Oak Ridge National Laboratory, C.K. Shih, The University of Texas, Austin

The thickness dependence of Au/Pb alloy formation on thin Pb quantum films is studied using *in-situ* low temperature STM/S. Sub-monolayer Au is deposited onto thin Pb films on Si(111) substrates. When Au deposition is carried out at low temperature (~100K), it is found that nano-islands with moire patterns form on top of Pb mesas. With annealing, these moire islands are transformed into three different types of Au/Pb surface alloys. Each type of alloy shows its unique electronic properties and can be clearly identified by STS. Interestingly, the formation of these alloys is directly related to quantum well states (QWS) of underlying Pb films. For thinner thicknesses of underlying Pb layers (below 12ML), it is also observed that the alloy formation probability has strong thickness preference.

2:40pm **SSI-ThA3 Far-From-Equilibrium Film Growth on Alloy Surfaces: Ni and Al on NiAl(110).** Y. Han, D. Jing, B. Unal, P.A. Thiel, J.W. Evans, Iowa State University

We have analyzed the deposition of Ni and Al on NiAl(110) surfaces by STM and by KMC simulation of multi-site atomistic lattice-gas modeling incorporating DFT energetics. The goal is to elucidate far-from-equilibrium growth of metal films on alloy surfaces, including self-growth of alloys. Deposition of Ni produces reversible formation of monolayer islands which have some preference for diagonal steps at 300K and which are distorted-hexagons at 400K. Deposition of Al at 300K produces irreversible formation of irregular monolayer islands perhaps favoring steps in the [-110] direction. These features are recovered by the modeling, which elucidates the distinct nature of terrace diffusion of Ni versus Al on NiAl(110), the details of island nucleation, and the complexity of edge diffusion which controls island growth shapes. Additional studies of sequential co-deposition reveal "history-dependent" structures far from perfect equilibrium alloy ordering. Depositing Al first then Ni creates monolayer islands with a core of Al surrounded by a ring of Ni (although intermixing may occur at the interface). In contrast, depositing Ni first then Al creates monolayer Ni islands with significant second layer population by Al (reflecting stronger binding of Al on top of the Ni islands versus on NiAl(110) according to DFT).

3:00pm **SSI-ThA4 Growth Instabilities on Cu Vicinals: Metallic Impurities.** R. Sathiyarayanan, University of Maryland, College Park, A. Bhadj Hamouda, University of Monastir, Tunisia, A. Pimpinelli, Univ. B-Pascal Clermont-2, France & Science Attaché, French Embassy, Houston, T. Einstein, University of Maryland, College Park

Spontaneous pattern formation through kinetically controlled epitaxial growth provides a viable route for nanostructuring of surfaces. Ernst and co-workers found that during growth, Cu(100) undergoes a mounding instability, and its vicinal surfaces develop a meandering instability.² More specifically, (i) the meandering wavelength (λ_m) scales with deposition rate (F) as $\lambda_m \sim F^{-\gamma}$, with $\gamma \approx 0.19$, (ii) both close-packed <110> and open <100> steps undergo meandering instability and (iii) above 10ML deposition, small pyramids appear near the steps. No previously-known instability mechanism, (esp. Bales-Zangwill, kink Ehrlich-Schwoebel effect, or unrestricted step-edge diffusion) could account for all of the experimental observations.

Using kinetic Monte Carlo simulations, A. Ben-Hammouda *et al.* showed that impurities codeposited on the surface could reproduce the λ_m - F scaling behavior and the formation of small pyramids.³ Further, they found that only those impurity atoms (i) whose bond to Cu adatom is about 1.6 times the strength of the Cu-Cu bond and (ii) whose diffusion barrier is about 1.6 times the barrier of Cu adatom could cause the observed instabilities. Due to their stronger bonds with Cu adatoms, impurity atoms hinder Cu adatom diffusion, thereby shortening the diffusion length and making λ_m less sensitive to deposition rate (F). Also, impurity atoms act as nucleation centers for the formation of small pyramids.

By computing the binding energies and diffusion barriers for certain candidate impurity atoms, we could eliminate several species as possible sources of the observed instabilities. Using density-functional theory

(DFT)-based Vienna *Ab-initio* Simulation Package (VASP), we computed the adsorption energies and diffusion barriers for many candidate impurity atoms. Our calculations show that common impurities such as oxygen, sulfur, and carbon actually repel Cu adatoms. The bonds formed by elements that alloy with Cu, e.g. Zn, Ag and Sn, are too weak to cause the observed instabilities; also, these atoms have smaller diffusion barriers than Cu. Our results indicate that either Fe or Mn atoms are causing the observed instabilities.⁴ We discuss the results of our calculations and the possible role of impurities in nanostructuring of surfaces.

¹Supported by NSF MRSEC Grant DMR 05-20471; NSF supported computer usage at NCSA, UIUC.

²N. Néel *et al.*, J. Phys.: Condensed Matter **15** (2003) S3227.

³A. Ben-Hammouda *et al.*, Phys. Rev. B **77** (2008) 245430.

⁴R. Sathiyarayanan *et al.*, in preparation.

3:40pm **SSI-ThA6 Epitaxial Thin Films and Multilayers: Growth Mode, Microstructure and Physical Property Correlations.** R.A. Lukaszew, College of William and Mary **INVITED**

The nucleation and growth mode of thin films determines their microstructure and also many of their physical properties, as for example the magnetic anisotropy in the case of epitaxial magnetic thin films. It is also possible to make artificial multilayers via deposition of subsequent layers of different materials and the microstructure and morphology of the intervening layers and interfaces determines many of the final structure properties.

Artificial metallic superlattices are multilayered thin films prepared by alternately depositing two or more elements epitaxially using ultra-high vacuum deposition or sputtering techniques. The concept of the superlattice was originally developed by physicists Leo Esaki and Raphael Tsu, who were both working at the IBM T. J. Watson Research Center in the 1960s.

Since then a wide spectrum of elements and compounds have been found suitable for deposition into multilayers and superlattice structures. The range of properties displayed by the resulting structures is greatly dependent upon the properties of both individual lattices as well as the interaction between them. For example, multilayers composed of magnetic and non-magnetic materials behave differently than the bulk materials and demonstrate a multiplicity of couplings between the magnetic layers. These couplings can be manipulated by choosing different layer materials and modifying their thicknesses. In fact the Giant Magneto Resistance (GMR) effect was found through such combinations and its discovery led to a Nobel Prize in Physics.

In this talk I will present our studies on nucleation and growth of metallic and magnetic layers and the correlation observed between their microstructure and some of their unique physical properties.

4:20pm **SSI-ThA8 Nucleation and Growth of Ceria-supported Pt-Au Bimetallic Nanoparticles.** Y. Zhou, J. Zhou, University of Wyoming

Ceria-supported metal particles have been under intensive study for their potential applications in fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the metal and ceria. Of particular interest are bimetallic systems because they can also exhibit unusual chemical and catalytic properties compared to the individual metals due to the synergistic effect between the two metals. To elucidate the nature of their chemistry in fuel cell applications, it is of significance to gain a fundamental understanding of their nucleation and growth processes on ceria supports. Here we report our recent study of bimetallic Pt-Au deposited on fully oxidized CeO₂(111) and reduced CeO_x(111) thin films using scanning tunneling microscopy and x-ray photoelectron spectroscopy. Ceria thin films with controlled degrees of cerium reduction were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Pt and Au were vapor-deposited onto ceria thin films. Our study demonstrates that the growth and sintering behavior of Pt-Au bimetallic particles is dependent on the Ce oxidation states, metal compositions, as well as the metal deposition sequence. The growth of Pt-Au on well-ordered CeO_x(111) thin films was compared to that of pure Pt and pure Au as well as to that of bimetallic Pt-Au supported on nanocrystalline ceria surfaces. The research is sponsored by the start-up fund at University of Wyoming and the Wyoming NASA Space grant.

4:40pm **SSI-ThA9 Growth of Iridium on Ge(111) Studied by STM and LEEM.** C. Mullet, S. Chiang, J. Morad, A. Durand, University of California, Davis

Iridium on germanium is a system which is useful for understanding the interaction of 5d metals with semiconductors, with potential applications to electronic contacts. We have used both scanning tunneling microscopy

(STM) and low energy electron microscopy (LEEM) to characterize the submonolayer growth of iridium onto Ge(111) as a function of coverage, deposition temperature, and annealing temperature. Ir deposited onto the Ge(111) c(2x8) surface forms a $(\sqrt{3}\times\sqrt{3})R30^\circ$ phase with the island size dependent upon substrate temperature during deposition. Deposition at a sample temperature of 670 C yields large micron-sized regions of continuous $(\sqrt{3}\times\sqrt{3})R30^\circ$ coverage, as seen by LEEM. Deposition at 400 C produces Ir islands of three different sizes, all of which are too small to be resolved in LEEM but can be easily observed in room temperature STM images: large islands of roughly 10 to 20 nm diameter, consisting of multiple layers; medium-sized islands of roughly 4 nm in diameter, and small islands about 1 nm in diameter. The medium sized islands show a preference for growing at the bottom edges of steps. The small islands show a nearly uniform distribution on the sample surface, with the interesting exception of preferentially ordering in arrays of lines connecting medium-sized islands. Heating the sample over 640 C yields islands of large enough size to be resolved with LEEM, with the island size dependent upon annealing temperature. Ostwald ripening was observed in LEEM movies. When these large islands form during sample heating, they appear to 'avoid' areas of high step density near surface defects. At 840 C, desorption begins from these types of regions.

5:00pm **SS1-ThA10 Adatom- and Addimer-Mediated Exchange Diffusion of Embedded Ge Atoms in the Ge/Si(001) Surface Alloy**, E. Bussmann, B.S. Swartzentruber, Sandia National Laboratories

Using low-bias empty-state STM images, we can resolve the location of embedded Ge atoms in the Ge/Si(001) surface alloy. We directly observe the diffusion of these embedded atoms at elevated temperatures ($>100^\circ\text{C}$). That the diffusion of the embedded Ge atoms occurs in time bursts, is spatially correlated, and results in long displacements implies that the process is defect mediated. The responsible defects are adsorbed monomers and dimers. We have identified two exchange-diffusion pathways for the movement of the embedded Ge atoms, both of which are consistent with previous first-principles calculations [1, 2]. Adsorbed monomers of Si or Ge can readily place exchange with surface atoms as they anisotropically diffuse along the substrate dimer rows. These monomer exchange events are strongly correlated with common trap sites for monomers, such as, the ends of dimer rows of islands. Less frequent events are associated with adsorbed dimers that can exchange one of their atoms with a surface atom. That is, an adsorbed Si-Si dimer can exchange one of its Si atoms with an embedded Ge atom to become a Si-Ge dimer, which can subsequently re-exchange the Ge atom into the surface at a different location. Because the barrier for exchange in both of these pathways is only slightly higher than that for diffusion, Ge deposition on Si(001) leads to intermixing and surface-alloy formation at any temperature where diffusion is active. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE, and was performed at the Center for Integrated Nanotechnologies, a U.S. DOE-BES user facility.

[1] Lu *et al.*, Surf. Sci. Lett., **506**, L282 (2002).

[2] Zipoli *et al.*, APL, **92**, 191908 (2008).

5:20pm **SS1-ThA11 Substrate Effect on the Morphological Transition of Planar Magic Ag Nanoclusters**, Y.P. Chiu, B.C. Huang, C.Y. Shen, National Sun Yat-sen University, Taiwan

Two-dimensional (2D) magic Ag nanoclusters have been demonstrated experimentally[1]. Experimental observations show that a template that originates from the electronic effect of quantum Pb islands grown on an Si(111) substrate can be used to develop Ag nanoclusters in planar feature with unusual size distributions, called a two-dimensional magic Ag nanocluster. Theoretically, the transition of Ag clusters from planar to 3D structures begins with Ag clusters of seven atoms without consideration of the substrate support [2]. However, utilizing the symmetry and size of the periodic pattern on the Pb islands, distinguishable planar hexagonal Ag clusters can be grown even for Ag clusters of 127 atoms [3]. How the substrate has influence on the morphological transition of Ag clusters from planar to 3D is of our interest and motivates the present work. To elucidate the effect of the substrate on the growth behavior of Ag clusters, highly oriented pyrolytic graphite (HOPG) is adopted as a template in the work. STM is used to characterize and analyze the growth behavior of Ag nanoclusters on HOPG. The process of the transition of Ag nanoclusters from planar to 3D and the onset of the formation of three-dimensional Ag clusters are also elucidated. A thorough analysis of the energetic optimization of Ag clusters not only yields information on the growth of Ag clusters on HOPG, but also elucidates how the substrate influences the formation of magic Ag clusters.

References

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[2] Eva M. Fernández, José M. Soler, Ignacio L. Garzón, and Luis C. Balbás, Phys. Rev. B **70**, 165403 (2004).

[3] Y.P. Chiu, C.M. Wei, and C.S. Chang, Phys. Rev. B Vol. **78**, 115402 (2008).

Surface Science

Room: N - Session SS2-ThA

Supramolecular Interfaces by Design

Moderator: Y. Chabal, University of Texas, Dallas

2:00pm **SS2-ThA1 Cyano-directed Self-assembly of n-modular Porphyrin Oligomers at Surfaces: The Delicate Balance Between Competing Interactions**, N.P. Reynolds, The University of Basel, Switzerland, L.-A. Fendt, ETH Zurich, Switzerland, M. Stöhr, N. Wintjes, M. Enache, The University of Basel, Switzerland, T.A. Jung, Paul Scherrer Institute, Switzerland, F. Diederich, ETH Zurich, Switzerland

The self-assembly properties of two cyano (CN) functionalized porphyrin isomers on Cu(111) were studied at different coverages by means of scanning tunneling microscopy (STM). Both isomers have two voluminous 3,5-bis(*tert*-butyl)phenyl substituents and two rod-like 4-cyanobiphenyl substituents in *cis* and *trans* configurations. For coverages up to one monolayer, the *cis* porphyrins were found to form a variety of oligomeric clusters ranging from dimers to hexamers, held together by cyanophenyl directed anti-parallel dipole-dipole interactions, hydrogen bonding and metal complexation. Furthermore, small changes in preparation conditions were also found to have a profound effect on the size distribution of the clusters. This variety and size distribution of the oligomers demonstrates how the delicate balance between the strength of adsorbate-adsorbate and adsorbate-substrate interactions has a major effect on self-assembly.

Previous work from Yokoyama *et al.*, using a similar molecule with shorter cyanophenyl binding groups formed exclusively tetrameric structures on less reactive Au(111) substrates. In this study high resolution STM images showed the presence of structures ranging from dimeric to hexameric, as well as chainlike structures. On the basis of this data we conclude that on the more reactive Cu(111), the very strong adsorbate-substrate interactions present are the dominating influence, leading to the multimorphism of binding motifs and oligomers observed.

[1] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **2001**, 413, 619-621.

2:20pm **SS2-ThA2 The Directed Assembly of TiOPc - C₆₀ Films: Three Structural Motifs**, Y. Wei, University of Maryland, S. Robey, National Institute of Standards and Technology, J. Reutt-Robey, University of Maryland

A key strategy for the improvement of organic electronic devices involves the optimization of chemical morphology on the interfaces of donor-acceptor heterojunctions for efficient charge separation. Fundamental studies of chemical morphology - electronic property relations, particularly along crucial domain boundaries, are needed to realize these goals. We present STM/STS studies of TiOPc: C₆₀ films, prepared in three dramatically different structural motifs: (1) Nanophase segregated TiOPc and C₆₀ domains, (2) A co-crystalline TiOPc₍₂₎ C₆₀₍₁₎ honeycomb network and (3) A regular array of triangular TiOPc domains and C₆₀ nanoclusters with a 10 nm repeat. Motif selection is accomplished through anisotropic TiOPc-TiOPc interactions, under the process control of TiOPc deposition rates. Subsequent C₆₀ deposition on these pre-engineered TiOPc films yields these three distinct structural motifs. Chemical morphology-electronic relations are then determined via Z (V) STS spectroscopy. Electronic transport gaps vary weakly (~0.2 eV) by C₆₀-TiOPc phase. Significantly, an ~0.5 eV increase in the transport gap appears along heterointerface boundaries. We present structural models for each hetero interface and discuss the physical origin of the observed transport characteristics.

This work has been supported by the National Science Foundation under Surface Analytical Chemistry grant CHE0750203 and the Dept. of Commerce through the NIST small grants program.

2:40pm **SS2-ThA3 Supramolecular Engineering in Two Dimensions, J.V. Barth**, Technische Universität München, Germany **INVITED**

The application of biologically inspired organization principles to artificial environments opens up intriguing vistas for the design of complex interfaces. Here we focus on well-defined metal surfaces serving as platforms to handle molecular building blocks with specific functionalities. We employ scanning tunneling microscopy for molecular-level imaging of both single molecules and self-assembled systems, whereas scanning tunneling spectroscopy captures the pertaining electronic properties. Distinct nanoarchitectures, such as biomolecular gratings, metal-organic arrays and porous nanomeshes, are realized through molecular recognition and selective hydrogen bonds, zwitterionic or metal-ligand interactions. Complementary insight from space-averaging techniques and computational modeling allows for the comprehensive assessment of structure-functionality correlation, notably including quantum confinement, chemical reactivity and magnetism. It is suggested that this supramolecular engineering strategy provides a versatile rationale to design unique nanosystems. Their tunable structural and functional characteristics bear promise for future technological applications.

3:40pm **SS2-ThA6 Functionalized C60 SAMs Diversity Via Molecular Conformation Variability, B. Diaconescu**, University of New Hampshire, T. Yang, Michigan State University, M. Jazdyk, G. Miller, University of New Hampshire, D. Tomanek, Michigan State University, K. Pohl, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule-substrate and intermolecular interactions. In order to control such self-organization processes, it is crucial to understand how this balance reflects onto the SAM's equilibrium structure. We will present a STM/DFT study of the self-assembly of C60 functionalized with alkyl chains of various lengths (F-C60) on Ag(111). We find that various structures are forming as a function of the alkyl chain lengths, ranging from zigzag to linear arrays of C60 cages, and they are driven by molecular conformational changes induced by the interaction with the surface. The symmetry of the F-C60 SAM is dictated by the molecular conformation, a consequence of molecule-surface interaction, while the size of the unit cell is a consequence of the intermolecular interactions. These results show that C60s can be assembled in 2D and non-compact molecular arrays with a unit cell symmetry and size controllable via appropriate chemical functionalization.

4:00pm **SS2-ThA7 Electronic Confinement Imposed by a Nanoporous Supramolecular Network, M. Matena, J. Lobo-Checa, M. Wahl**, University of Basel, Switzerland, H. Dil, University of Zürich, Switzerland, L.H. Gade, University of Heidelberg, Germany, T.A. Jung, Paul Scherrer Institute, Switzerland, J. Zegenhagen, ESRF, France, M. Stöhr, University of Basel, Switzerland

Molecular assemblies on surfaces can be used as templates that allow the study of host guest interactions and provide in a further step an ideal starting point for the generation of more complex hierarchic structures. An important prerequisite besides the regularity of such structures is their stability.

We reported the formation of a molecular honeycomb network generated by thermal dehydrogenation of a perylene derivative (DPDI) on a Cu(111) surface [1]. By thermal activation, these molecules become H-bond donors/acceptors and form a highly regular honeycomb structure which is commensurate to the Cu substrate. This network can be used as a template for the incorporation of guest molecules in its hexagonal "holes" [2], [3]. Besides utilizing this network for the study of guest molecules, XSW (x-ray standing wave) experiments were carried out to gain more structural information and by this more information on the molecule substrate interaction. This is done by determining the vertical height of the molecules above the Cu surface before and after annealing the sample. Before annealing, the DPDI molecule is chemisorbed. It mainly interacts via its N atoms with the Cu surface and is in a bridge-like configuration. After annealing, the height difference between the end groups and the perylene core is lowered what is required to enable H-bonding between the molecules.

Furthermore, to study the interaction between the electronic Cu surface state and the DPDI network, scanning tunneling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES) were used. Each pore of our porous network confines the Cu surface state in what can be described as a 0D quantum dot. Due to the imperfect confinement observed for all 0D cases studied so far on surfaces, the quantum dots couple with their neighbors resulting in shallow dispersive electronic bands [4]. A consequence of this work is the perspective to engineer these artificially

created electronic structures by modification of the dimensions of the molecular network periodicities together with the appropriate choice of the substrate.

[1] M. Stöhr et al., *Angew. Chem. Int. Ed.* 44 (2005) 7394; [2] M. Wahl et al., *Chem. Commun.* (2007) 1349; [3] M. Stöhr et al., *Small* 3 (2007) 1336; [4] J. Lobo-Checa et al., submitted.

4:20pm **SS2-ThA8 Surface Supported Chain Formation of Magnetic Molecules, S. Chang**, University of Hamburg, Germany, K. Clark, A. Dilullo, Ohio University, S. Kuck, University of Hamburg, Germany, S.-W. Hla, Ohio University, G. Hoffmann, R. Wiesendanger, University of Hamburg, Germany

The last years showed a tremendous development into accessing and understanding the physics of metal-organic complexes in contact to a surface on a single molecule level. Molecular classes in the focus are often specialized but commercially available systems. Further progress towards device development requires molecular classes with a more flexible structure for functionalization.

In our contribution we introduce such a promising candidate, the so called Salens, and present first results on the local investigation by Scanning Tunneling Microscopy (STM). Salens are volatile metal-organic complexes with the metallic ion caged from three sides. Salens are chemically easily modified to tune the interaction with a substrate, with neighboring molecules, or to establish an intramolecular electronic and magnetic communication between two metallic centers through the organic periphery. Based on the paramagnetic Co-Salen, which shows no self-assembly on metallic substrates, we demonstrate that the exchange of a single atom in the molecular structure the interaction can be tuned from repulsive to attractive interaction[1]. Even surface-supported covalent bonding can be initiated to form larger entities. By means of STM, STS, and STM induced manipulation we will discuss the adsorption and the electronic properties of the parent Co-Salen and modified Salens on metallic and isolating surfaces.

Acknowledgements: This work was supported by the DFG within the GrK 611 and the SFB 668-A5, by the EU in the project "SPiDMe", and the NSF-PiRE program.

[1] S. Kuck et al., "Steering two dimensional molecular growth via dipolar interaction", accepted for publication in *ChemPhysChem* (2009).

4:40pm **SS2-ThA9 Reactive Adsorption to Ordered Bis-Terpyridine Networks, T. Waldmann, H.E. Hoster**, Institute of Surface Chemistry and Catalysis, Germany, D. Künzel, Institute of Theoretical Chemistry, Germany, M. Roos, A. Breitruck, Institute of Surface Chemistry and Catalysis, Germany, A. Groß, Institute of Theoretical Chemistry, Germany, R.J. Behm, Institute of Surface Chemistry and Catalysis, Germany

Using time resolved scanning tunneling microscopy, we tested the effect of O₂ exposure on ordered supra-molecular networks of Bis-terpyridine derivative molecules (2,4'-BTP)[1,2] supported on Au(111)[3], Ag(111) [3,4] and Graphite[3] (HOPG) substrates at T = 300 K. Under certain circumstances, our image sequences unambiguously show modifications of individual 2,4'-BTP molecules upon O₂ exposure and concomitant rearrangements within the hydrogen bonded adlayer. Furthermore, comparison of the behaviour on different substrates clearly shows that these modifications require a catalytically active surface.

The experimental observations are complemented by density functional theory calculations. In combination, both give rise to a probable model for the observed surface reactions and their effect on the supramolecular structure.

[1] U.Ziener et al., *Chem.Eur.J.* 8, 951, 2002

[2] C. Meier et al., *J.Phys.Chem.B* 109, 21015, 2005

[3] H.E. Hoster et al., *Langmuir* 23, 11570, 2007

[4] M.Roos et al., *Phys. Chem. Chem. Phys.* 9, 5672, 2007

5:00pm **SS2-ThA10 Charge Transfer-Driven Molecular Self-Assembly at Organic/Metal Interfaces, T.-C. Tseng**, Max Planck Inst. for Solid State Res., Germany, C. Urban, W. Yang, Univ. Autonoma de Madrid, Spain, R. Otero, UAM & IMDEA-Nano, Spain, S.L. Tait, Max Plank Inst. for Solid State Res., Germany, M. Alcamí, D. Ecija, M. Trelka, Univ. Autonoma de Madrid, Spain, J.M. Gallego, ICMM-CSIC, Spain, M.A. Herranz, Univ. Complutense de Madrid, Spain, F. Martín, Univ. Autonoma de Madrid, Spain, N. Martín, Univ. Complutense de Madrid, Spain, K. Kern, Max Plank Inst. for Solid State Res., Germany, R. Miranda, UAM & IMDEA-Nano, Spain

Organic heterostructures based on blends of molecules with electron-accepting (large electron-affinity) and electron-donating (small ionization

potential) character display interesting electrical and optical properties with promising technological applications. For example, they show electroluminescence for Organic Light Emission Diodes (OLEDs), photovoltaic response for solar cell devices and one-dimensional conduction for low molecular-weight metallic films, while strong acceptors or donors are the basis for metal-organic magnets. These blends of molecules are deposited onto or contacted with metallic layers and their performance depends crucially on the alignment of energy levels, the molecular nanostructure and crystalline perfection. Interfaces between organic species with either donor or acceptor character and metal surfaces are, thus, of paramount importance for the performance of the devices described above. This observation has motivated a large effort aimed at understanding the electronic structure of organic/metal interfaces and, in particular, the alignment of the energy levels at the interface related to the charge transfer between the organic donor or acceptor species and the metallic surface. Charge transfer, however, not only leads to modifications in the alignment of energy levels; usually, it is also related to structural transformations in both donating and accepting species. Unfortunately, too often it is assumed that the substrate is just an inert spectator, playing no active role in the supramolecular organization. We describe here experiments (STM, LEED, XPS) and theoretical simulations that unequivocally demonstrate that for strong charge transfer systems, such as the organic acceptor tetracyanoquinodimethane (TCNQ) deposited on Cu(100) *both* the molecules *and* the substrate suffer strong structural rearrangements that may even control the resulting molecular ordering. Such charge transfer-induced structural rearrangements at both sides of the organic/metal interface might have significant effects on the subsequent growth and structure of the organic film and, thereby, on device performance.

5:20pm **SS2-ThA11 Architectural Complexity, Intermolecular Interactions, and Charge Transfer in Supramolecular Networks at Surfaces**, *H. Adler, Y. Ge, S.L. Tait*, Indiana University

Self-assembly of two-dimensional supramolecular networks stabilized by hydrogen bonding or metal—organic coordination offers an efficient route to the rational design of functional surface architectures and provides a model system for (bio-)molecular assembly. These systems may contribute to advances in sensors, catalysis, molecular electronics, photovoltaics, and other thin film device applications. Such systems have been demonstrated to form highly-ordered, extended networks by selective and directional coordination bonding. Experiments were made using metal atoms and organic ligands containing carboxylic acid, cyano or pyridyl functional end groups, which were vapor deposited to atomically clean and flat surfaces. Structural characterization by scanning tunneling microscopy allows molecular level insight into the structure and assembly of the systems. X-ray photoelectron spectroscopy provides evidence for chemical interactions within the networks. High-resolution electron energy loss spectroscopy lends insight into intermolecular interactions. These experiments are correlated with density functional theory calculations for a better understanding of the bonding interactions that stabilize the highly ordered surface nanostructures. Binary mixtures of ligands allow for a large variety of metal-organic frameworks based on hierarchical assembly, co-crystallization, or cooperative multi-ligand coordination interactions. Current studies are focusing on understanding chemical function of these systems and how this can be tuned through supramolecular design strategies.

Thursday Afternoon Poster Sessions

Surface Science

Room: Hall 3 - Session SS-ThP

Surface Science Poster Session

SS-ThP1 Ordered 2-D Structure of Si(337)-4×1 Induced by C Incorporation into Si(5 5 12)-2×1, H. Kim, O. Dugerjav, G. Duvjir, H. Li, J.M. Seo, Chonbuk National University, Republic of Korea

Using STM, it has been found that Si(5 5 12)-2×1 composed of tetramer (T) / dimer-adatom (D-A) rows and π -bonded (π) / honeycomb (H) chains [Surf. Sci. **601**, 1831 (2007)] is transformed irreversibly to an ordered (337)-4×1 terrace with (113) facets through adsorbing C₂H₂ at 650°C followed by post-annealing at 750°C. The transformation from (5 5 12) to (337) starts from a T row and a π chain in the (5 5 12) surface, and simultaneously the rest part of (5 5 12) converts to T rows and π chains, which will be transformed to (337). By Si 2p and C 1s core-level photoemission studies using synchrotron radiation, it has been confirmed that such an irreversible structural transformation is due to subsurface C atoms. If the (337) terrace is only composed of T rows and π chains with a 2× periodicity, the compressive stress exists so that the (337) terrace becomes unstable. However, subsurface C atoms release this compressive stress through breaking 1-D structures and change to a stable surface composed of 4×1 dot structures. The detailed atomic structures of the 4×1 surface and the steps of transformation will be presented.

SS-ThP2 Surface Passivation by Sb Adsorption: Sb/Si(114)-2 × 2, O. Dugerjav, H. Kim, G. Duvjir, H. Li, J.M. Seo, Chonbuk National University, Republic of Korea

Sb adsorption on the Si(114)-2×1 surface [composed of dimer (D), rebonded-atom (R), tetramer (T) rows] at 600 °C has been investigated by STM and synchrotron photoemission spectroscopy (PES). When the Sb coverage exceeds 0.25 ML, two periods of 2×1 [(D-R-T)-(D-R-T)] is transformed to 2×2 [D-R-D-R-R_{Sb}-D-R_{Sb}, where R_{Sb} means an R row replaced by deposited Sb atoms]. Such a transformation turns out to be nanofaceting to 2×(115) and 2×(113) and is originating from the stress balance between the tensile rebonded D_B-type D(6)-R(5)-D(6)-R(5) rings [Phys. Rev. Lett. **77**, 687 (1996)] and the compressive R_{Sb}(5)-D(7)-R_{Sb}(5) rings [Surf. Sci. **411**, 54 (1998)]. This Sb-adsorbed 2×2 surface has 37.5% less dangling bonds and 0.27 eV less band-bending than the clean surface. It has been found that the addimer adsorbs exclusively on the D(7)-R_{Sb}(5) ring site, which implies that the critical condition for addimer adsorption is the relative angle between dangling bonds of D(7)-R_{Sb}(5) rings.

SS-ThP3 In situ Attenuated Total Reflectance and Transmission Fourier Transform Infrared Spectroscopy of (tetrakis(dimethylamido)hafnium (IV) Decomposition and Adsorption Dynamics on H-Si(100) Surface, K. Li, N. Li, T.M. Klein, The University of Alabama

Low temperature atomic layer deposition (ALD) is favored for more uniform thin film. The authors have investigated the surface reaction mechanism of first step of Hf ALD agent tetrakis(dimethylamido)hafnium (TDMAH) reacting on the H-Si(100) surface for low temperature range 60-250°C by *in situ* ATR-FTIR. The formation H-Hf species was observed in the chemisorbed layer and a gas phase initiated adsorption mechanism was hypothesized by *ab initio* calculation. *In situ* transmission FTIR will be used to monitor the gas phase decomposition dynamics and products of TDMAH. Two most possible reactions: insertion and β -hydride elimination are expected to be observed. Deuterium water prepared background will be used to verify the Hf-H species on H-Si(100). Interfacial bonds of Hf-N and Hf-Si are to be of about 1:1.5 in concentration from thermodynamic calculation. Minor C-Si bond from silylation by product is expected to be observed during desorption. Experimental measurement of decomposition rate will be compared with the *ab initio* kinetic data.

SS-ThP4 Exploring Photomechanically Switching Molecules on Semiconductor Surfaces, J. Cho, L. Berbil-Bautista, N. Levy, D. Poulsen, J.M.J. Fréchet, M.F. Crommie, UC Berkeley

The photomechanical switching behavior of organic molecules changes dramatically when the molecules are placed on a surface. Metal surfaces, for example, often quench or slow photomechanical activity due to strong molecular interaction with continuum electronic degrees of freedom. Semiconductor surfaces are expected to induce very different molecular switching behavior due to the presence of a band gap, potentially resulting in longer excited-state lifetimes and enhanced control of photomechanical properties. We have explored the local structure and self-assembly of photomechanical molecules on the semiconducting GaAs(110) surface

using variable temperature scanning tunneling microscopy. We will report on the nanoscale response of azobenzene derivatives on GaAs to optical irradiation in the UV-vis spectral regime.

SS-ThP5 Photo-induced Reactions of Alanine Adsorbed on Permalloy: A Real Time X-ray Photoelectron Spectroscopy Study, V. Kalyanaraman, R.A. Rosenberg, Argonne National Laboratory, P.J. Ryan, Ames Laboratory, M. Abu Haija, Argonne National Laboratory

Recently it was demonstrated that chiral selective chemistry can be induced by spin-polarized electrons from a magnetic substrate. The C-O bond cleavage rate in adsorbed 2-butanol showed a 10% enhancement depending on the chirality of the molecule and spin polarization of the substrate secondary electrons(1). We have recently extended this research to alanine (CH₃CHNH₂COOH), the simplest chiral amino acid. Our initial work examined the x-ray induced photolysis of alanine adsorbed on a thick Permalloy film by monitoring changes in the C1s and N1s photoelectron spectra as a function of irradiation time. Alanine was shown to adsorb in both zwitterionic (~2/3) and neutral (~1/3) forms on Pd(111)(2). C1s and N1s x-ray photoelectron (XP) spectra of alanine adsorbed on Permalloy at 200 K indicate similar adsorption behavior. Irradiation of the adsorbate with x-ray photons results in changes in both the C1s and N1s XPS data, which we attribute to C-C bond fission at the chiral carbon desorbing CO₂ and/or CO from the COO- moiety, and leaving behind ethylamine and/or HCN. Strong support for this assignment comes from similar intensity variations in the C 1s and N 1s XP spectra from D-alanine on Pd(111) as the substrate temperature was increased above room temperature(2). Future work will be devoted to determining if the observed x-ray induced reaction rates are sensitive to the alanine chirality and the polarization of the secondary electrons from the underlying substrate.

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

References

- (1) R. A. Rosenberg et al., Phys. Rev. Lett. **101** (2008) 178301.
- (2) Feng Gao et al., Surf. Sci. **601** (2007) 3276.

SS-ThP6 Trajectories and Neutral Fractions of Alkali Ions Scattered from Au(788), R.E. Lake, M.P. Ray, C.E. Sosolik, Clemson University

Stepped metal surfaces are natural systems for studying lateral quantum confinement [1]. Au(788) is a surface vicinal to the (111) plane that reconstructs and forms stable 3.8 nm wide periodic monatomic steps with (111) orientation. Step edges terminate in {111} microfacets. Electron wave functions are confined laterally in a direction perpendicular to the steps and contribute a 1D-like quantum well state to the Au(111) electronic structure. To probe this structure-property relationship we scatter hyperthermal energy alkali ions from the surface and measure the energy and neutral fraction of the scattered ions. By analyzing our data with the classical trajectory simulation SAFARI, ions scattered from the steps can be clearly distinguished from the step edge scattering events. The neutral fraction of scattered alkali ions is sensitive to the electrostatic potential directly above a scattering site and can detect quantum confined states [2]. Measured neutral fractions for different species of alkali ions are interpreted with a model of multi-state resonant charge transfer.

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[2] G. F. Liu, Z. Sroubek and J. A. Yarnoff. Phys. Rev. Lett. **92**, 216801 (2004).

SS-ThP7 Probing Diffusivity in Nanoscale Supercooled Liquid Films using Rare-Gas Atoms, J. Mathiesen, R.S. Smith, B. Kay, Pacific Northwest National Laboratory

Molecular beams, temperature programmed desorption, and infrared spectroscopy were used to study the diffusivity in nanoscale supercooled liquid films of alkanes and alcohols. Amorphous films were grown on top of a layer of rare-gas atoms on a Pt(111) substrate at 25 K in UHV. As the films are heated they transform from amorphous to supercooled liquid films around the glass transition temperature. The rare-gas atoms were found to diffuse through the films in the supercooled liquid state. In a series of experiments, the layer thickness and heating rate were varied to extract diffusivities over a range of different temperatures. Numerical simulations of the rare-gas atoms diffusing through the supercooled films were used to quantitatively model the experimental results. Mixing of initially layered isotopically labeled alcohol and alkane films were also performed. The extracted diffusivities for the rare-gas atoms were in good agreement with the self-diffusion coefficients extracted from the experiments with

isotopically labeled species. The details of the experiment and the interpretation of the results will be discussed in detail.

The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

SS-ThP8 Adsorption of Metal Phthalocyanines on Cu(111) and Cu(100): A STM Study, S. Chang, J. Brede, J. Schwöbel, S. Kuck, G. Hoffmann, R. Wiesendanger, University of Hamburg, Germany

The temperature dependent adsorption behavior of 4-fold symmetric metal phthalocyanines (MPcs) on metals with commensurate and incommensurate symmetries was investigated by means of scanning tunneling microscopy. On the 4-fold symmetric Cu(100) surface, planar and 4-fold molecular structures in two equivalent orientations were found for MPcs when prepared at room temperature. In addition, two metastable orientations were identified when prepared at low temperature which can be depopulated upon annealing. MPcs adsorbed on the 6-fold symmetric Cu(111) surface showed a disturbed molecular appearance. The symmetry of molecular structures changed from 4-fold to 2-fold which is discussed in terms of molecule-substrate interaction.

This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project "SPiDMe".

SS-ThP9 Iron Phthalocyanine on the Ag(111) Surface: Structure and Electronic States, K.W. Higgs, T. Takami, C.E. Carrizales, Washington State University

Epitaxial growth of iron phthalocyanine on a silver (111) surface has been studied with scanning tunneling microscopy in ultrahigh vacuum. Commensurate two-dimensional ordering with parallelogram unit vectors (**b**₁, **b**₂) where **b**₁ = 5**a**₁ + 2**a**₂ and **b**₂ = 5**a**₂, where **a**₁ and **a**₂ are unit vectors of Ag(111) surface, were observed. The parallelogram structure was more commensurate than those of FePc on Au(111) or graphite and of CuPc on Ag(111), and the surface density is greatest on Ag(111). The orbital mediated tunneling spectra showed a first ionization potential at 5.1 eV, similar to that in cobalt phthalocyanine on Au(111) surface.

SS-ThP10 Adsorption, Self Assembly, and Electronic States of Corrole Molecules Adsorbed on Different Copper Facets, L. Lichtenstein, S. Kuck, G. Hoffmann, R. Wiesendanger, University of Hamburg, Germany

A new member of the metalloporphyrinoid class is the one-carbon short corrole which is a very accessible, easily tunable compound with many potential applications in material science and catalysis. These molecules differ from the parent porphyrin molecules [1] mainly by their lower inherent symmetry and the smaller cavity. In this study using STM we address the conformation (orientation and chirality) and self assembly of iron-triphenylcorrole (FeTPC) molecules on Cu(100) and Cu(111). At low coverage FeTPC molecules show restricted symmetry and can be controllably switched among different conformations [2]. At higher coverage formation of regular aggregates can be observed. We will present the results of the growth study in dependence of surface geometry and coverage and discuss results of scanning tunneling spectroscopy investigations of these systems.

[1] W. Auwärter et al., "Molecular nanoscience and engineering on surfaces", Int J. Nanotechnology Vol. 5, 1171 (2008).

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This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project "SPiDMe".

SS-ThP11 One and Two Dimensional Structures of Water on Cu(110) and O/Cu(110)-(2x1) Surface, B.Y. Choi, Y. Shi, M. Salmeron, Lawrence Berkeley National Laboratory

The interaction of water molecules with single crystalline surfaces provides a model for a fundamental understanding of the wetting properties of metals. We investigate one and two dimensional water structures on a clean and on an oxygen precovered Cu(110) surface using scanning tunneling microscopy and non-contact atomic force microscopy. In previous work it has been proposed that at sub-monolayer coverage water forms pentagon based chain-like structure on the clean Cu(110) surface at low temperature. Water pentagons have a strong water-metal interaction as well as a minimal strain in hydrogen bond¹. On an oxygen precovered Cu(110) surface, hexagonal based honeycomb structures are preferred to form along the Cu-O stripes. However, it is not clear whether the hexamers are composed of intact or half-dissociated water molecules². We will discuss how the Cu-O

stripes affect the formation of the honeycomb structures and chains of water pentamers.

¹J. Carrasco et al Nature Mater. 8, 427 (2009)

²J. Ren et al Phys. Rev. B 77, 054110 (2008)

SS-ThP12 Evaporation and Sliding of Water Droplets on Hydrophobic Coatings with Nanoscale Roughness, T. Furuta, A. Nakajima, Tokyo Institute of Technology, Japan, M. Sakai, KAST, Japan, T. Isobe, Tokyo Institute of Technology, Japan, Y. Kameshima, Okayama University, Japan, K. Okada, Tokyo Institute of Technology, Japan

Hydrophobic coatings have been used widely to apply for various engineering products. For assessing these properties, static wettability such as the contact angle or sliding angle is not always a useful criterion for materials design. Recently, the recognition of the importance of dynamic wettability such as droplet's sliding velocity or acceleration on a tilted surface has been growing gradually.

Water droplets are known to slide down on the hydrophobic solid surface by a caterpillar-like rolling motion with or without slippage at the solid-liquid boundary; a direct observation method for internal fluidity of sliding water droplets was established recently using particle image velocimetry (PIV). The contribution ratio of rolling and slipping motions to overall sliding acceleration reportedly depends on nanoscale roughness and chemical heterogeneity of the hydrophobic coatings.

On the other hand, evaporation is a fundamental phenomenon for liquids. Various studies have been conducted in relation to this phenomenon for liquid droplets on solid surfaces. Ultra-small, e.g. nanoliter-scale, droplets are evaporated and disappeared in a short time, which corresponds to a situation of large volume change ratio per unit period. It might possess similar dependence against nanoscale surface heterogeneity as well as dynamic wettability.

We prepared fluoroalkylsilane coatings with different nanoscale roughness. This study examined evaporation (including nanoliter-scale droplets) and sliding behaviors of water droplets on these coatings using an automatic microscopic contact angle meter and PIV method.

Evaporation and sliding behaviors of water droplets were investigated on smooth and rough coatings. Evaporation behaviors for these two coatings differed when nanoliter-scale droplets were used, although they were nearly identical for microliter-scale droplets. The droplets on the smooth coating exhibit greater sliding acceleration and a larger slipping velocity ratio than those on the rough coating. Both the evaporation behavior of nanoliter-scale droplets and sliding velocity of microliter-scale droplets were affected by nanoscale surface heterogeneity.

Moreover, considering power balance around the three phase contact area, line tension was measured for microliter-scale and sub-nanoliter-scale droplets of an ionic liquid on a highly smooth and homogeneous fluoroalkylsilane coating. Values for microliter-scale droplets were two orders larger than those for sub-nanoliter-scale droplets despite their identical combinations of solid surfaces and liquid. Scale factors related to this measurement and from the liquid play an important role in the discrepancy.

SS-ThP13 Passivation of Al(111) with Organic and Inorganic Adlayers, T. Yamada, RIKEN, Japan, M. Kawai, The University of Tokyo, Japan

Passivation of clean Al(111) has been attempted against oxidation in O₂ or air at room temperature by various kinds of adlayers prepared on the surface. The goal of this attempt is to block the growth of oxide layer by introducing a covering monolayer or thin multilayer, whose thickness is smaller than 1 nm. Metallic aluminum surfaces stored in air are usually covered with more than a few nm of Al oxide layer, which prevent us from fabrication of nanostructures and nanoparticles of pure metallic Al. If an ultrathin passivation layer, composed of inorganic or organic materials in a controlled manner, can inhibit oxidation of Al substrate, it will help enhancing the accuracy and precision of nano-scale fabrication. This approach was successful in passivating Si wafer surfaces [1]. When a clean Al(111) surface was exposed to pure O₂ gas at room temperature, the surface was covered with an amorphous oxide layer observed by low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [2]. The thickness of oxide layer was calculated from XPS signal intensities, with referring to spectra of a cleaned sapphire (γ -Al₂O₃) surface. The process of oxide accumulation was once saturated below $\sim 10^{-1}$ Torr of O₂ pressure, at which the thickness of oxide layer was <0.5 nm. Formation of such oxide layers was blocked with various kinds of thin adlayers, such as fluoride thin layers, alkanethiol monolayers etc., similarly to the formerly reported C₆₀ layer [3]. At O₂ pressures higher than 10⁻¹ Torr, another sort of rigorous oxidation process took place. The thickness of oxide layer was approximately proportional to the logarithm of O₂ exposure, reaching a few nanometers. Most of the monolayers from small precursor compounds

could not block this process of oxidation. This process seems to involve penetration of O atoms deeply into the Al substrate. Practically, it is desirable to inhibit this rigorous process of oxidation. In this talk, we will present our attempts using monolayers including long linear molecules anchored on Al(111). The oxidation process was examined in the air up to the atmospheric pressure, involving O₂ and H₂O. Some kinds of adlayers on Al(111) were vulnerable in contact with H₂O. It is probably important to involve hydrophobic compounds to build a firm, oxidation-resistant monolayer.

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SS-ThP14 Reduction of Friction Drag by Superhydrophobic / Superhydrophilic Coatings, M. Sakai, Kanagawa Academy of Science and Technology, Japan, *A. Nakajima,* Tokyo Institute of Technology, Japan
Recently, the importance of controlling wettability on the solid surface is recognized in various industries. In the current paper, we evaluated friction drag of water on various surfaces including superhydrophobic / superhydrophilic coatings. The amount of friction drag was evaluated by the decrease of hydrostatic pressure during flowing in the tubes coated by various materials. When Reynolds number is smallest, superhydrophobic coating provides small friction drag. On the other hand, a superhydrophobic coating provided smallest friction drag when Reynolds number is 6000. The mechanism of this difference was discussed from the viewpoints of fluid mechanics and surface materials science.

SS-ThP15 Dynamic Solid-liquid Interaction on Hydrophobic Surfaces, N. Yoshida, The University of Tokyo, Japan, *M. Sakai,* Kanagawa Academy of Science and Technology, Japan, *A. Nakajima,* Tokyo Institute of Technology, Japan, *T. Watanabe,* The University of Tokyo, Japan

Dynamic solid-liquid interaction as a liquid droplet-movement on inclined hydrophobic~superhydrophobic surfaces was investigated. The liquid droplet movement was affected by a surface energy, roughness, and homogeneity of the solid surface, and furthermore it is revealed that the internal fluidity detected by Particle Image Velocimetry method changed the movement. On hydrophobic surfaces, the movement simply depended on contact angle if the solid surface had chemically and physically homogeneity. Surface inhomogeneity caused increases of contact angle hysteresis and internal fluidity, and then the droplet movement was observed to be decreased. In this presentation, we will discuss about the detail of relations among them.

SS-ThP16 Surface Reaction of Ozone with Alkali Halide Salts, T. McIntire, J. Taing, University of California, Irvine, *P. Ashby,* Lawrence Berkeley National Laboratory, *R.L. Grimm, A. Margarella, M.H. Cheng,* University of California, Irvine, *Z. Liu,* Lawrence Berkeley National Laboratory, *J.C. Hemminger,* University of California, Irvine

Heterogeneous reactions involving the oxidation of the halide components of sea-salt aerosols with trace atmospheric gases (e.g., ozone, hydroxyl, and NO_x) have been proposed to be responsible for the release of active halogen species into the gas phase. While such halogen containing species have been observed in the marine boundary layer by field studies, the detailed mechanisms of the heterogeneous reactions leading to halogen release from sea salt aerosols are not well understood. In this work, reactions of gas phase ozone with alkali halide single crystals were studied at varying ozone and water vapor concentrations. Changes in the alkali halide salts were measured using transmission FTIR, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). While previous investigations found single crystals of KI oxidize to form a passivating layer of KIO₃ crystallites, the present study notes the loss of reactants with no observed surface-phase oxidized species, AFM experiments show that ozonolysis of KBr single crystals leads to roughening of step edges and the formation of etch pits which appears to depend on the amount of water vapor present. XPS spectra show a decrease in interfacial bromide believed to be concomitant with the etching observed in the AFM studies. Implications for the role of water on the reaction of gases such as ozone with alkali halide single crystals are discussed.

SS-ThP17 Evolution of Microscopic Surface Deformation on Si(111) due to Low Energy Ion Bombardment, P. Piercy, J.M. David, D. Pohl, University of Ottawa, Canada

Low energy ion bombardment of a crystalline solid may cause a variety of surface and subsurface damage. At moderately elevated sample temperatures to prevent amorphization, the sputtering process may leave a step-and-terrace morphology, but surface reconstruction may be disordered

and a distribution of ion-induced defects may remain in a shallow, inhomogeneously strained, subsurface layer. After low energy argon ion bombardment on Si(111), we use a spot profile analysis of low energy electron diffraction data at in-phase conditions to measure a low amplitude, continuous distribution of surface height, which occurs in addition to atomic-height steps and other short-range atomic disorder at the surface. Measurements over a range of ion dose, ion energy, and sample temperature, are attributed to surface deformation due to strain around subsurface defects. For bombardment of the Si(111) surface at 600K by 230 eV argon ions with dose increasing in the range 10¹⁵-10¹⁶ cm⁻², we find a continuous surface height distribution, whose contribution to the interface width increases from hundredths of an Angstrom up to ≈ 0.1 Å, correlated laterally over tens of Angstroms. These results may be interpreted in terms of an elastic continuum model of the solid, with defects created below the surface by independent ion bombardment events modeled simply by a distribution of small inclusions. At a higher surface temperature of 800 K, the surface deformation after the same ion energy and doses as above gives interface width contribution *w* increasing to 0.07 Å; with further bombardment to a dose of 10¹⁷ cm⁻², *w* grows to 0.15 Å. At a higher ion beam energy of 730 eV, *w* increases to a saturation value of 0.18 Å after an argon ion dose of ≈ 2·10¹⁶ cm⁻². Implications for the evolution of the buried defect distribution will be discussed.

SS-ThP18 Ordering Mechanisms of Stripe Arrays on B-doped Si(100), I. Ermanoski, N.C. Bartelt, G. Kellogg, Sandia National Laboratories

We have used low energy electron microscopy (LEEM) to study in real time the self-assembly of periodic stripe arrays on atomically flat Si(100) with high boron doping. Stripes consist of extremely elongated vacancy islands of single atomic height, formed at ~900°C, confined in micrometer-sized pits. We have been able to create highly ordered arrays of straight, parallel stripes (in pits of up to ~8 μm in size) formed by allowing various defects to heal over relatively long periods of time. To allow this equilibration to occur, sublimation was compensated for by an external Si doser, allowing observation of stripe evolution over the course of hours, with no net loss or gain of Si from the area of interest. Equilibrium stripes are very uniform in width and periodicity, and exhibit the greatest stability at 0.5 monolayer coverage. Observed stripe formation and ordering mechanisms include spontaneous nucleation and growth of new stripes, longitudinal splitting, as well as coarsening due to surface diffusion. Stripe periodicity depends on temperature, allowing for control of this property. Stripes form in a temperature range of ~100C, outside of which they assume the familiar shape of elongated islands. Stripe order can be preserved to room temperature by quenching.

Work supported by the U.S. DOE, Office of BES, DMSE. Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's NNSA under Contract No. DE-AC04-94AL85000.

SS-ThP20 Degradation of Semiconductor Photoelectrode Surfaces in Aqueous Environments from ab-initio Molecular Dynamics, B. Wood, T. Ogitsu, E. Schwegler, Lawrence Livermore National Laboratory

Among currently known approaches for hydrogen production, catalytic splitting of water molecules using semiconductor-based photoelectrochemical (PEC) devices has garnered particular interest, with reasonably high efficiencies already demonstrated in laboratory conditions. Unfortunately, these materials often evidence extremely facile surface corrosion, severely limiting their practical use in real-world devices. Currently, a clear understanding of this corrosion process at the water-semiconductor interface and its damaging effect on catalytic activity is lacking. Although certain theoretical efforts have attempted to address this issue, these studies have generally focused on zero-temperature gas-phase molecular adsorption, forgoing a realistic model of the liquid-solid interface. Accordingly, we have performed extensive *ab-initio* molecular dynamics simulations to probe the structure, chemistry, and dynamics of the water-electrode interface for model semiconductor systems in a realistic aqueous environment. Our work has focused on InP and GaAs, which, although structurally and functionally similar, exhibit substantial differences in terms of stability in an aqueous environment and in surface reactivity. These calculations are able to provide a unique in-depth understanding of surface

structure and transport. As such, they promise to provide a crucial first step towards understanding the complexities of the atomistic processes involved in hydrogen evolution and PEC corrosion.

Friday Morning, November 13, 2009

Surface Science

Room: M - Session SS1-FrM

Nanoclusters, Organics and Beam Induced Chemistry

Moderator: J. Zhou, University of Wyoming

8:20am **SS1-FrM1 Site-specific Adsorption of C60 on Au(111)**, X. Zhang, L. Tang, Q. Guo, University of Birmingham, UK

The well-known herringbone reconstruction of the Au (111) surface consists of a regular array of line dislocations, which may act as nucleation sites for metals or organic materials [1, 2]. In this study, we reveal for the first time the selective adsorption of C60 molecules at the elbow sites on Au(111). Deposition of submonolayer of C60 molecules onto a Au(111) surface at room temperature usually leads to the co-existence of three structures [3]. In recent experiments we observed site-selective adsorption of individual C60 molecules, which show an obvious preference for nucleating at the elbows of the x type dislocation lines. As coverage increases, compact C60 islands are observed to form on the FCC regions between two neighboring C60 molecules. Interestingly, only about 50% of the elbow sites are active in mediating the formation of these nanometre sized C60 islands. The observed site-specific adsorption and nucleation is interpreted based on findings from high resolution STM imaging which reveals the atomic scale structure of the surface defects around the elbow sites.

Another site-selective adsorption phenomenon was observed after depositing C60 molecules onto parallel gold stripes (gold-fingers) [4], which were fabricated from monoatomic gold steps by high tunnelling current STM scanning. These gold-fingers have different kinds of microfacet ($\{111\}$ and $\{100\}$) on their two parallel steps. The C60 molecules prefer to adsorb on the less stable $\{100\}$ steps and form close packed islands, while the $\{111\}$ steps only have their FCC regions been occupied by the molecules. Besides the energy difference, the different underlying herringbone patterns of the two steps may also be a key factor leading to site-selective adsorption to the gold fingers.

References:

1. I. Chado et al., Appl. Phys. Lett. 226 (2004) 178.
2. T. Yokoyama et al., Nature 413 (2001) 619.
3. X. Zhang, R.E. Palmer and Q. Guo, Surf. Sci. 602 (2008) 885.
4. Q. Guo, F. Yin and R.E. Palmer, Small 1 (2005) 76-79.

8:40am **SS1-FrM2 Epitaxial Growth of Organic Nanocrystals with Antiferroelectric Stacking**, M. Trelka, A. Medina, C. Urban, C. Claessens, Universidad Autonoma de Madrid, Spain, R. Otero, UAM & IMDEA-Nano, Spain, J.M. Gallego, ICMM-CSIC, Spain, T. Torres, Universidad Autonoma de Madrid, Spain, R. Miranda, UAM & IMDEA-Nano, Spain

Organic nanoparticles display size-dependent absorption and fluorescence bands and single photon emission. The detailed understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement. A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are much weaker than molecule-substrate interactions, thus promoting a layer-by-layer growth mode, and preventing the fabrication of isolated 3D nanocrystal.

Here we show that, upon deposition of cone-shaped subphthalocyanine (SubPc) molecules on Cu(111), isolated triangular nanocrystallites up to 3 ML high appear on the surface before the completion of the first monolayer. The different molecular layers show an alternating or antiferroelectric (AF) stacking of the molecular dipole moments. The structure of such nanocrystals can be explained by the joint effect of electrostatic (dipole-dipole) and dispersive (π - π) interactions. Although 1 ML-thick islands can also be found on the surface, the molecular arrangement in these areas is different from the geometry of the 1st-layer molecules in the crystallites. We

suggest that the formation mechanism of the organic nanocrystals is related to the existence of two different adsorption geometries, cone-up and cone-down, each of which sits on different molecular layers placed at different distances from the surface upon crystallite formation.

9:00am **SS1-FrM3 Trapping Dynamics on Complex Surfaces: Organic Thin Film Growth on Surfaces Terminated with Self-Assembled Monolayers**, T.V. Desai, A.R. Woll, S. Hong, K.J. Hughes, J.R. Engstrom, Cornell University

A significant challenge in fabricating organic thin film transistors is that of controlling and understanding the properties of the interface between the organic semiconducting layer and the dielectric. It has been observed that charge transport can be affected significantly by chemically altering the dielectric surface with self-assembled monolayers (SAMs). However, the effects of the molecular scale interactions between the organic molecule and the substrate remain unclear. Diindenoperylene (DIP) is a promising candidate for applications in organic thin film electronics owing to the ability to form highly ordered films with excellent electrical properties. Here, using supersonic molecular beam techniques and *in situ* real time synchrotron X-ray scattering, we have examined the adsorption dynamics of DIP on silicon dioxide (SiO₂) and SiO₂ modified with a number of SAMs. These SAMs included octadecyltrichlorosilane (ODTS), octyltrichlorosilane (OTS), fluorooctyltrichlorosilane (FOTS), and hexamethyldisilazane (HMDS), representing a range of molecular sizes and chemical terminations (-CH₃ vs. -CF₃). In this work, we make use of x-ray intensity oscillations at the so-called anti-Bragg position to extract the occupation (coverage) of the individual layers as a function of time. These coverage-exposure relationships give us a direct measure of the (relative) probabilities of adsorption as a function of coverage. For the conditions examined (E_i = 5.1-12.3 eV, T_s = 40 °C) on all the starting surfaces (SiO₂ and SAM/SiO₂) we observe a decrease in the probability of adsorption with increasing incident energy indicative of trapping-mediated adsorption. The probability of adsorption on these starting surfaces is dependent on both the chain length and the chemical composition of the SAM, where the probability of adsorption is greatest on the thickest organic layer, ODTS, followed by OTS, SiO₂, FOTS, and HMDS. Once all surfaces are covered by DIP, however, the effects of incident kinetic energy are greatly reduced, and trapping is very efficient over the range of kinetic energies examined. For organic layers of comparable chemical composition and density, the initial probability of adsorption depends strongly on the layer thickness, where trapping on ODTS is most efficient, and on HMDS, least efficient. In a selected set of cases we will compare our experimental results with recent results from molecular dynamics simulations to obtain insight into the possible molecular-scale mechanisms/events that may occur in these systems. One such event appears to be the undeniable role of direct molecular insertion into the thicker organic layers such as ODTS.

9:20am **SS1-FrM4 Real-time Microscopic Investigations of the Growth of Thin Organic Films**, J.T. Sadowski, Brookhaven National Laboratory, A. Al-Mahboob, Y. Fujikawa, T. Sakurai, Tohoku University, Japan

The growth mode, morphology, crystallinity and electronic structure of thin rubrene (5,6,11,12-tetraphenylnaphthacene: C₄₂H₂₈) films grown in ultra-high vacuum (UHV) conditions have been studied *in situ* in the low-energy electron microscope (LEEM).

Rubrene is attracting a considerable attention since it has shown promise in OTFT's, with field-effect mobilities of the single-crystal FET devices surpassing that of amorphous silicon and even pentacene. However, still little is known how the electronic and chemical properties of the substrate affect the crystallinity of rubrene thin films.

When rubrene is deposited on clean semiconductor surfaces, such as Si(111)-7x7, it reacts with the dangling bonds, partially dissociating and forming a disordered wetting layer. The nucleation of the crystalline islands follows, but high nucleation density and slow surface diffusion, due to a rough and disordered interface, result in a poor crystallinity of the films.

A completely different growth mechanism is observed upon rubrene deposition on semi-metallic Bi(0001) surface. In this case rubrene islands nucleate immediately, without formation of any wetting layer. Keeping the substrate temperature at 400K results in nucleation of large, single-crystalline rubrene islands preferentially oriented along the surface terraces. Low-energy electron diffraction (LEED) patterns indicate formation of a new rubrene phase. Most interestingly, this phase is characterized by chiral ordering of the molecules within single crystalline domains having sizes in the range of tenths of micrometers. Such chiral ordering has a great potential for improvement of the crystallinity of rubrene films, and thus performance of rubrene-based devices.

9:40am **SS1-FrM5 *In Situ* Characterization of Surfaces Following Soft and Reactive Landing of Complex Ions.** Q. Hu, P. Wang, P.L. Gassman, J. Laskin, Pacific Northwest National Laboratory

Soft- and reactive landing (SL/RL) of mass-selected ions enables highly selective preparation of uniform thin films of a variety of complex molecules on surfaces. We have recently demonstrated covalent immobilization of several model peptides on the self-assembled monolayer (SAM) of N-hydroxysuccinimidyl ester terminated alkythiol on gold (NHS-SAM) using RL. Another remarkable finding is that SL and RL can be utilized for purification of peptide conformations that may not be stable in solution on SAM surfaces. For example, while Ac-Ala₁₅-Lys peptide mainly exist in its β -sheet conformation in solution, SL and RL of this peptide on the surface results in immobilization of a very stable α -helical conformation. This study presents a pathway for preparation of conformationally-selected peptide arrays that cannot be prepared using traditional solution-phase approaches. Here we present SL of singly and doubly protonated peptides (Gramicidin S, Substance P, Ac-Ala₁₅-LysH⁺ and Ac-LysH⁺-Ala₁₅) onto inert SAMs of alkythiol (HSAM) and fluorinated alkythiol (FSAM) on gold, and RL of singly protonated diamines and multiply protonated dendrimers onto reactive NHS-SAM and COF-terminated SAM surfaces. The modified SAM surfaces were characterized using *in situ* real time infrared reflection absorption spectroscopy (IRRAS) and secondary ion mass spectrometry (SIMS). *In situ* analysis of substrates during and after the SL/RL processes is essential for understanding charge transfer phenomena, reactivity of soft-landed molecules, and modification of the secondary structure of the molecule as a result of interaction with the surface.

10:00am **SS1-FrM6 Surface Deposition and Characterization of Cu Clusters Utilizing Soft-Landing Drift Tube Spectrometry.** G.F. Verbeck, S. Davila, University of North Texas

Intro

The soft-landing of ion cluster onto a surface is a novel approach for the deposition of specifically selected cluster. Our approach differs from current deposition/ soft landing techniques in that it allows specific molecule to be landed with a KE of around 1-5 eV where current soft-landing techniques are in the range around 30 - 50 eV. Large KE may not be ideal for the landing of metal clusters as the energy is translated into motion along the surface resulting in aggregation along defects in the surface. We have recently developed soft-landing system using a drift tube, high pressure (1 - 100 torr), and a modified substrate to create a soft-landing around 1 - 5 eV. Surface modifications can isolate clusters and protect them from aggregation. This soft-landing method allows for the characterization of a specific soft landed metal cluster on the surface via AFM, Raman Spectroscopy, and Electrochemistry.

Method

Our soft-landing instrument allows for the direct ablation of metal samples via laser or atmospheric plasma. Laser ablation of a metal sample by a pulsed Nd:YAG laser for duration of 1-3 hrs acts as our source for ion clusters. The instrument is operated at a pressure between 1-13 torr, with a voltage between 10-500 \pm V that is applied uniformly across the drift tube. Helium is used as a buffer gas and acts as a means to control cluster formation. The high pressure narrows the clusters KE from 40 eV to about 1 eV through collisions via the buffer gas. Clusters travelling within the drift tube are separated based on collisional cross-section. A pulsed split ring assembly at the end of the drift tube isolates specifically selected clusters directly on an unprepared or modified surface. The sample surface is then removed for characterization.

Data

Drift Tube spectra collected at 8 torr shows a cluster range of $n = 1-8$ along with corresponding Cu_nO. Clusters that have been landed on the surface are characterized using AFM. Images show an aggregation of the clusters in a striation patterns along the surface. The bridging across a defect instead of deposition within has also been seen. This clustering, aggregation, and growth shows a soft-landing has been made on the surface keeping the Cu cations and clusters intact. Self assembly of specifically isolated cluster groups has also been shown to occur on the surface of mica. Other characterization methods and various clusters may be specifically selected and landed with time allowing further development.

Instrument operates at pressure/temperature closer to ambient conditions than currently available, allowing ions to be soft landed on various modified surfaces for isolation and characterization.

10:20am **SS1-FrM7 Plasma Induced Interfacial Reaction of Hafnium Nano Particle and SiO₂ Film for Direct HfSiON Growth.** T. Kitajima, T. Nakano, National Defense Academy, Japan, T. Makabe, Keio University, Japan

In the paper, we show the example of the non-thermal chemistry over the nano-metal/semiconductor interface caused by the non-equilibrium low pressure RF plasma exposure. The process is directed to the new fabrication scheme of high-k dielectric thin film for MOSFETs with fewer process steps, lower impurity, and minimized EOT (equivalent oxide thickness). In the process, high density hafnium metal nano particle with 4 nm diameter is formed on SiO₂/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with SiN interfacial layer.

Current ULSI technology requires the use of hafnium related high-k dielectrics with ~3 nm thick for MOSFET to lower the power consumption. HfSiON is the most applicable chemistry for the high-k material with proper energy band alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO₂ utilizing the thermal interfacial reaction was previously proposed [1]. The process demonstrates remarkably low impurity in the film due to the lack of carbon in contrast to the case of MOCVD processes. In our

case, 2.5 nm thick Hf metal layer is deposited with e-beam deposition source on SiO₂/Si(100) surface uniformly. The morphology obtained with the in-situ non-contact AFM measurement revealed the surface consists of the high density array of Hf nano particles with the size of 4 nm in diameter. The exposure of atomic nitrogen and ions from the non-equilibrium plasma enables the introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS analysis. The following plasma exposure (~10min.) enables the diffusion of Si atoms into the high-k film from the underlying SiO layer. The Si content in the film increases with the exposure time and becomes comparable to the Hf content with 35 min. exposure. The XPS spectrum shows the Si incorporated is mostly nitrided in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

[1] H. Watanabe, Appl. Phys. Lett. 85, 449 (2004).

10:40am **SS1-FrM8 Modeling Thin Film Deposition Processes in an HDP-CVD Reactor.** A. Bhoj, K. Shah, ESI US R&D, Inc., M. Megahed, ESI Group, Inc., P. Kothnur, R. Kinder, Novellus Systems, Inc.

Modeling HDP-CVD processes for high quality dielectric film deposition in high aspect ratio device structures remains a challenging task. A number of details such as the reactor geometry, inductive and capacitive power deposition, gas-phase chemistry and surface kinetics need to be addressed in a coupled manner. In this multi-physics approach, a reactor scale model in conjunction with a feature scale model is used to investigate the process dependence of deposition rates across the wafer and within features. Plasma properties, gas flow and deposition at the walls are addressed in the reactor scale model. The resulting film growth inside microscopic trenches is captured in the feature scale model. The reactor geometry is similar to that described in an earlier publication [1]. Data for gas phase and surface reaction kinetics are obtained from published literature [2]. In an earlier work [3], trends in deposition rate at the wafer with inductive power were discussed. In this paper, the impact of reactor scale process parameters such as bias power deposition, gas flow rates and wafer temperature on deposition at the wafer are investigated, and modeling results are compared to experimental data [4].

[1] M. Tuszewski and J. A. Tobin, *J. Vac. Sci. Technol. A* **14**, 1096 (1996).

[2] E. Meeks, *et al*, *J. Vac. Sci. Technol. A* **16**, 544 (1998).

[3] A. Bhoj, *et al*, *EuroCVD and CVD XVII, 216th Meeting of the Electrochemical Society*, Vienna, Austria (2009).

[4] A. Bhoj, P. Kothnur, and R. Kinder, *61st Annual Gaseous Electronics Conference*, Dallas, TX (2008).

11:00am **SS1-FrM9 Ion Scattering Studies of Isolated Au Nanoclusters**, *S. Balaz, J.A. Yarmoff, R.D. Gann*, University of California, Riverside

Isolated Au nanoclusters are grown atop amorphous solid water (ASW) at low temperature. This process, which represents the first step in the growth of nanoclusters via the buffer layer assisted growth (BLAG) method, is a unique way in which to fabricate small deposited clusters that have minimal interactions with a substrate. Such clusters are able to serve as model systems for investigations of how nanocluster electronic structure depends on shape and size. Low energy alkali ion scattering was used to probe the atomic and electronic structures of the clusters *in situ*. ASW was first deposited as a separation layer onto SiO₂/Si(111) at liquid nitrogen temperature, and then Au was evaporated onto the ASW to form nanoclusters. The mean size of the clusters is expected to increase with increased Au deposition. Time-of-flight (TOF) spectroscopy was used to collect charge-resolved spectra of scattered 2 keV ⁷Li⁺ and ³⁹K⁺ ions. Spectra collected following small Au depositions display only a sharp single scattering peak, while multiple and plural scattering features are present following larger depositions. The change in spectral shape is indicative of the formation of multilayer nanoclusters. The experimental findings are interpreted with the aid of Monte-Carlo ion scattering simulations. The neutral fraction of scattered K⁺, which provides an indication of the filled quantum states, starts at ~50% for small Au coverages and decreases with further deposition, indicating changes in the quantum state occupancy with cluster size. The lack of any angular dependence to the neutralization implies that the clusters behave as atomic-like structures. Further experiments will investigate how the clusters evolve when deposited onto the substrate by heating to desorb the ASW layer.

11:20am **SS1-FrM10 Initial Nucleation and Growth of Oxide Scale on Haynes® 214® Alloy**, *V. Shuthanandan, S.V.N.T. Kuchibhatla, A.S. Lea, Z. Zhu, M.H. Engelhard, S. Thevuthasan*, Pacific Northwest National Laboratory, *P. Singh*, University of Connecticut, *V. Deodshumukh*, Haynes International, Inc., *H. Ghezelayagh*, Fuel Cell Energy, Inc.

A combination of ion beam and electron spectroscopy techniques have been used to precisely understand the initial oxidation of a multicomponent alloy system, Haynes®214®. Surface sensitive nature of these techniques has been rightly exploited to precisely identify different phases formed at different times of oxidation. Haynes® 214® is a high temperature, Ni-Cr-Al-Fe based alloy, widely used in a plethora of applications ranging from “clean firing” of ceramics to the gas turbine industry. Various reports exist in the literature, which describe the long term stability of this alloy under oxidizing environments at temperatures above 900°C. *Despite the number of applications and significant interest in this alloy, a clear mechanism of the early stage oxidation has not been documented.* An effort is underway to estimate the initial nucleation and growth of oxide scale on this alloy in various environments (such as dry and humid air). A combination of ion and electron based techniques such as Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), particle induced x-ray emission (PIXE), secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to measure the initial nucleation of the oxide scale on this alloy. NRA was used to track the oxygen depth profile while PIXE and RBS were used to track the changes in matrix components of the alloy for the formation of oxide scale for as-low-as 1 min of oxidation. Chemical analysis of this early stage of oxidation formation was studied by AES and XPS. Chemical surface mapping obtained from Auger analysis indicated that the initial oxide formed is chromia which is completely dominated by alumina after 7 min of oxidation treatment at 900°C in air. Various merits of this work will be discussed along with possible future scope for using Ion beam techniques for processes such as oxidation of metals, a most widely studied problem.

Surface Science

Room: N - Session SS2-FrM

Semiconductor Surfaces and Interfaces II: Si

Moderator: C.L. Hinkle, University of Texas at Dallas

8:20am **SS2-FrM1 Observation of Realtime Oxidation of Si(111) Surfaces using Second Harmonic Generation**, *K. Gundogdu, B. Gokce, E.J. Adles, D.E. Aspnes*, North Carolina State University

Realtime material diagnostics during material growth is commonly used in industrial applications. Linear optical methods specifically spectroscopic ellipsometry (SE) probe thin film thickness with a nanometer precision by measuring the change in dielectric susceptibility during material growth. However SE is a spatially averaging technique and therefore can not probe

the chemical change at the bond level. In this work we show that second harmonic generation experiments can be used to directly visualize changes in interface and surface bonds in realtime, providing a powerful bond structure characterization tool. We employed SHG experiments to probe the oxidation of hydrogen terminated Si(111) surfaces. We are able to extract the oxidation rates for different bonds on Si(111) surfaces that are nominally flat and with vicinal cut. We found that the initial hydrogen termination process effects the oxidation rate in the bond level. We compare the results of SHG measurements with that of spectroscopic ellipsometry.

8:40am **SS2-FrM2 Surface Passivation Mechanism of Atomic Layer Deposited Al₂O₃ Films on c-Si Studied by Optical Second-Harmonic Generation**, *N.M. Terlinden, J.J.H. Gielis, V. Verlaan, G. Dingemans, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, it was shown that Al₂O₃ thin films synthesized by (plasma-assisted) atomic layer deposition (ALD) provide excellent surface passivation of *n*, *p* and *p*⁺ type *c*-Si as highly relevant for *c*-Si photovoltaics. It was found that a large *negative* fixed charge density (up to 10¹³ cm⁻²) in the Al₂O₃ film plays a key role in the passivation mechanism of Al₂O₃ [1, 2]. The surface passivation quality of Al₂O₃ strongly increases with film thickness before reaching saturation around 10 nm as determined by carrier lifetime spectroscopy. In this contribution a study into the thickness effect will be presented in order to distinguish between the influence of field-effect passivation, *i.e.* electrostatic shielding of charge carriers by the fixed negative charge, and chemical passivation, *i.e.* by a reduction of the interface defect density. To this goal the nonlinear optical technique of second-harmonic generation (SHG) has been utilized. SHG is highly surface and interface specific and allows for the contactless determination of internal electric fields ($\geq 10^5$ V/cm⁻¹). Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range, has revealed a thickness independent electric field for Al₂O₃ films with thicknesses ranging from 2 to 20 nm. This implies that the field-effect passivation is not affected by the film thickness and that the thickness dependence in passivation quality can be attributed to a changing level of chemical passivation. Moreover, this result confirms that the fixed negative charges are located at the Al₂O₃ interface as also indicated by conventional C-V measurements. In addition, SHG shows clear differences between measurements performed on Al₂O₃ films grown by thermal and plasma-assisted ALD. These are likely related to the properties of the interfacial SiO_x induced by either growth process. The presence of this oxide is suggested to be responsible for the chemical passivation quality. Furthermore, the differences indicate a smaller contribution of field-effect passivation for the Al₂O₃ grown with thermal ALD compared to the film from the plasma-assisted process. These results have led to a deeper understanding of the *c*-Si surface passivation by Al₂O₃ as will be discussed.

[1] B. Hoex *et al.* *J. Appl. Phys.* **104**, 044903 (2008)

[2] J.J.H. Gielis *et al.* *J. Appl. Phys.* **104**, 073701 (2008)

9:00am **SS2-FrM3 Influence of Alkali-Metal Adsorption on Phase Transition of In/Si(111)-4 × 1 Surface**, *H. Shim, W. Lee, G. Lee*, Inha University, Republic of Korea, *S. Yu, J. Koo*, Korea Research Institute of Standards and Science

One monolayer of In on a Si(111) surface forms 4×1 structure at room temperature (RT). This In/Si(111)-4×1 surface has a quasi- one dimensional (1D) metallic electronic structure and undergoes a symmetry-lowering phase transition into an insulating 8×2 phase at low temperature (LT) upon cooling the sample below approximately 130 K [1]. Adsorption of Na atoms on the surface was reported to convert the 4x1-RT phase into the 8×2-LT phase even at RT [2]. We investigated using low-energy electron diffraction (LEED) the influence of alkali-metals (Na, K, Li) adsorption on the structural phase transition of this quasi-1D In/Si(111) surface. Introducing the alkali metals with low coverage on the surface at room temperature was found to affect the 4×1-to-8×2 structural phase transition by lowering the transition temperature (T_c). The T_c decreased almost linearly and the transition becomes more rounded when the amount of deposited alkali-metals atoms was increased. The decrease of T_c with the increase of the amount of adsorbed Na atoms is suggested to be due to the doping of electrons from adsorbates to the substrate [3]. In the high-coverage regime, new superstructures appear in LEED with the adsorption of alkali metals. Comparison of the adsorbate-induced superstructures in low-coverage and high-coverage regimes will be made and discussed.

[1] H. W. Yeom, *et al.*, *Phys. Rev. Lett.* **82**, 4898 (1999)

[2] S. S. Lee, *et al.*, *Phys. Rev. Lett.* **88**, 196401 (2002)

[3] H. Shim, *et al.*, *Appl. Rev. Lett. in press* (2009)

9:20am **SS2-FrM4 The First Attachment of Polybutadiene and Functionalized Polybutadiene to Hydrogen-Terminated Silicon, with Post-Derivatization of these Adsorbed Species**, *E. Nelsen, T. Wickard*, Brigham Young University, *H. Schlaad*, Max Planck Institute of Colloids and Interfaces, Germany, *R.C. Davis, M.R. Linford*, Brigham Young University

We report the first attachment of polymers with pendant vinyl groups to hydrogen-terminated silicon(111) (Si(111)-H) under mild conditions; 1,2-addition polybutadiene (Mw 3200-3500) in solution was attached to Si(111)-H at room temperature with only visible light activation. We also report the partial functionalization, in solution, of 1,2-addition polybutadiene with various thiols using thiol-click chemistry and the subsequent attachments of these compounds to Si(111)-H. The partially functionalized polybutadienes allow further functionalization at the surface through their unreacted carbon-carbon double bonds, as demonstrated with a perfluorinated thiol. We present this as a useful strategy for silicon surface modification. Surfaces were characterized with contact angle goniometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM).

9:40am **SS2-FrM5 Mechanistic Study of Photochemical Grafting of Alkenes to Group IV Semiconductors**, *X. Wang, J. Streifer, P. Colavita, R.J. Hamers*, University of Wisconsin-Madison

The grafting of organic molecules on semiconductor surfaces initiated by UV light has become an efficient means to tailor the chemical and physical properties of surfaces of materials, enabling their integration with various applications of the devices. *In situ* photoelectron yield experiments were performed in the spectral range from 3 to 6 eV on alkene liquid/nanocrystalline diamond (NCD) interfaces. *N*-Alkenes carrying different terminal functional groups: trifluoroacetamide-protected 1-aminodec-1-ene (TFAAD) and 10-*N*-Boc-aminodec-1-ene (tBoc) were used to investigate the dependence of photoelectron yield on the energy of the molecular acceptor level. Amorphous carbon was used in addition to NCD to study the influence of the substrate electronic structure on the photoelectron yield threshold. The photochemical attachment of TFAAD on H-terminated NCD surfaces at various incident photon energies was characterized by X-ray photoelectron spectroscopy (XPS) to investigate the correlation between the excitation energy and the reaction efficiency. These measurements reveal that the photochemical reaction on carbon surfaces is initiated via the photoejection of electrons from the solid valence band into the acceptor levels of the alkenes. SEM images of patterned molecular layers on two H-terminated single crystal diamonds (SCD, type Ib and IIb) with different hole mobilities reveal much sharper transition between functionalized and non-functionalized regions on the sample with much lower hole mobility (type Ib SCD). However, the surface coverage of grafted alkenes as characterized by XPS is quite similar on these two surfaces. These data imply that while the photoemission of electrons controls the reaction efficiency, the holes left in the substrates can diffuse and control the grafting sites.

Recent data exploring the mechanism on silicon will also be presented. Our comparison of silicon and diamond suggests that there are some common factors underlying the ability to graft alkenes onto various semiconductors, but also some important differences. These results suggest that photochemical grafting may be broadly applicable to a wide range of materials, and that a fundamental understanding of the mechanism facilitates the design and synthesis of well defined functional interfaces.

10:00am **SS2-FrM6 Structure and Order of Organophosphonate Self-Assembled Monolayers on Si(100)**, *M. Dubey, T. Weidner, L.J. Gamble, D. Ratner, D.G. Castner*, University of Washington

Organophosphonic acid self-assembled monolayers on oxide surfaces have seen growing use in electrical and biological sensor applications [1-2]. Molecular order in organophosphonic acid SAMs is highly desirable for reproducible electronic properties of these modified surfaces. In this regard, packing and order of the SAMs is important, as it influences the electron transport measurements. In this study, we examined the order of the phosphonate films deposited on silicon oxide surface by the Tethering By Aggregation and Growth (T-BAG) method [3] using various state-of-art surface characterization tools. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy is used to study the order of a methyl- and hydroxyl- terminated phosphonate SAMs in vacuum and sum frequency generation (SFG) spectroscopy is used to study their order in aqueous condition. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) on these samples confirm the presence of chemically intact monolayer phosphonate films. NEXAFS spectroscopy confirmed a considerable degree of molecular order in the octadecylphosphonic acid (ODPA) and 11-hydroxyundecylphosphonic acid (PUL) films with a tilt angle of 37° and 47° respectively. *In situ* SFG studies in deuterated water were conducted to determine the order of these films

under biologically relevant conditions. The ODPA film showed the peaks for terminal methyl units, which are expected for ordered films. PUL films also showed a considerable degree of alignment indicated by resonances of the methylene unit next to the terminal hydroxyl group. These studies indicate that well ordered SAMs with methyl or hydroxyl termination can be prepared on oxide surfaces using phosphonate headgroups. These surfaces can be subsequently used to anchor biomolecules for biomaterial and biosensor applications.

[1] A. Cattani-Scholz, D. Pedone, M. Dubey, S. Neppel, B. Nickel, P. Feulner, J. Schwartz, G. Abstreiter, M. Tornow, *ACS Nano* **2008**, 2, 1653.

[2] H. Klauk, U. Zschieschang, J. Pflaum, M. Halik, *Nature* **2007**, 445, 745.

[3] E. L. Hanson, J. Guo, N. Koch, J. Schwartz, S. L. Bernasek, *Journal of the*

American Chemical Society **2005**, 127, 10058

10:20am **SS2-FrM7 Hydrogen-bond Mediated Chemistry of Glycine on Si(111)7×7: A Catch-And-Release Approach to Surface Functionalization**, *K.T. Leung*, University of Waterloo, Canada

The growth of glycine film by thermal evaporation on Si(111)7×7 at room temperature has been studied by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). In contrast to the common carboxylic acids, glycine is found to adsorb on the 7×7 surface through dissociation of the N-H bond (instead of the O-H bond). The presence of a transitional adlayer between the first adlayer and the zwitterionic multilayer is identified by its characteristic N 1s XPS features attributable to intermolecular N-to-HO hydrogen bond. An intramolecular proton transfer mechanism is proposed to account for the adsorption process through the amino group. We also demonstrate that the observed transitional adlayer can be used as a flexible platform to “catch-and-release” biomolecules with compatible H-bonding active sites in a controllable and reversible manner. Intricate evolution of the surface adsorption arrangement during the initial growth has also been monitored by STM. Early evidence of collective assembly of glycine into novel structures in the nanometer length scale could be found.

10:40am **SS2-FrM8 Site-selective Reactivity of Ethylene on Si(001) induced by Local Electronic Distortions**, *G. Mette, C.H. Schwalb*, Uni Marburg, Germany, *M. Dürr*, Hochschule Esslingen, Germany, *U. Höfer*, Uni Marburg, Germany

The adsorption of organic molecules on semiconductor surfaces is of special interest with respect to surface functionalisation and its use in molecular electronics. Due to the localized electronic states of a semiconductor surface, its reactivity strongly correlates with the local electronic properties of the dangling-bond states. Dissociative adsorption of H₂ on Si(001), e.g., shows pronounced site-selective reactivity at steps or preadsorbed atomic hydrogen [1].

In this study, we test the concept of site-selective reactivity at locally distorted configurations for more complex, organic molecules. On that account, the adsorption of ethylene on clean and hydrogen precovered Si(001) surfaces has been investigated by means of scanning tunneling microscopy. On the clean surface, two ethylene adsorption geometries were identified with ethylene adsorbed on one and two dimers, respectively. The latter adsorption geometry shows significantly lower reactivity and has not been observed so far. Preadsorption of atomic hydrogen and the concomitant distortion of the electronic states is found to increase the reactivity of this two-dimer adsorption pathway by almost two orders of magnitude. Its site selective reactivity thus surpasses that of the one dimer configuration on the clean surface.

The results are rationalized in the framework of a precursor mediated adsorption process. Our experiments indicate that the conversion barrier between precursor and final chemisorbed state can be efficiently controlled by changing the local electronic structure of the surface. Thus, locally distorted dangling-bond configurations allow for the control of site-selective reactivity also in the case of barrierless, non-dissociative adsorption of an organic molecule.

[1] M. Dürr and U. Höfer, *Surf. Sci. Rep.* 61, 465 (2006)

11:00am **SS2-FrM9 Identifying Adsorbate Structures on Semiconductor Surfaces Using Simulated Scanning Tunneling Microscope Images**, *L. Yang, D. Doren*, University of Delaware

Simulated Scanning Tunneling Microscopy images, based on first-principles calculations, have been used to characterize adsorption products of organic molecules on semiconductor surfaces and assign molecular structures to specific features in experimental STM images. Three examples are presented: 1) Styrene molecular lines on the H-terminated Si(100)-2x1 surface system exhibit several novel molecular conductance phenomena. First-principles calculations show that the phenyl ring orientation at chain

ends are fluxional, favoring structures with the terminal ring arranged perpendicular to the molecular line. Simulated STM images show that the tunneling current depends strongly on the phenyl ring orientation, since it controls the coupling between the charged dangling bond and the styrene π system. The perpendicular orientation shows higher conductivity than the parallel one, increasing the apparent height of the molecule at the end of the row. This is consistent with experimental observations, while the simulated images of the parallel-ring geometry are not. Because such subtle changes in molecular structure control the flow of electrical currents, STM can be used to distinguish these conformations. 2) The bonding configuration of styrene attached to the bare Si(111)-7x7 surface is not known from spectroscopic measurements, though two likely possibilities have been identified. Matching simulated empty-state and filled-state STM images to new experimental observations provides strong evidence that the attachment of styrene to Si(111)-7x7 is by a [4+2] cycloaddition, involving both the external $-\text{CH}=\text{CH}_2$ and a $\text{C}=\text{C}$ inside the phenyl ring. A comparison experimental images to theoretical predictions of the bias dependence for the two binding structures is critical to this identification. 3) Three unsaturated organic molecules – styrene, phenyl acetylene, and benzaldehyde – were attached to the H-terminated Si(111) surface through analogous radical chain reactions. Both simulated and experimental STM images of the three molecules show significant differences in apparent height, despite small differences in physical height. Thus STM is sensitive to the functional group used to link the molecule to the surface. The simulations also suggest a new scanning protocol that can enhance the contrast among molecules. The so-called “local constant height” STM images, which probe the spatial variation of conductance, show distinctive features for the three molecules that can be used to tell the molecules apart very easily.

11:20am **SS2-FrM10 Defect Engineering via Modification of Semiconductor-Oxide Interfaces**, *P. Gorai, Y. Kondratenko, E.G. Seebauer*, University of Illinois at Urbana-Champaign

The behavior of defects within silicon can be changed significantly by controlling the chemical state at nearby surfaces or solid interfaces. Experiments have shown that certain chemical treatments change the ability of a free surface to act as a “sink” for point defects such as interstitials. When the surface is made chemically active, this ability rises. The surface can then remove Si interstitials selectively over impurity interstitials and such behavior can be kinetically quantified through an annihilation probability. Although annihilation probabilities for interstitials have been measured under various conditions for free surfaces, very little understanding exists for the corresponding quantity at solid-solid interfaces. Understanding of interface influence on interstitial annihilation is very important in fabrication of advanced transistors for post-implantation damage removal and dopant activation. The present work seeks to develop scientific understanding of interface activity for Si interstitial annihilation and measure the annihilation probabilities at interfaces between silicon and several kinds of oxides and nitrides. Diffusion of isotopically labeled Si (mass 30) in Si host lattice was used as a marker for elucidating how changes in the Si-SiO₂ interface affected Si self-diffusion after annealing. Marked differences are observed among the various interfaces. Continuum simulations of the measured SIMS profiles were subsequently employed to quantify annihilation rates at the Si-SiO₂ interface.

Authors Index

Bold page numbers indicate the presenter

— A —

Abdulgalil, A.G.M.: SS1-WeA2, 29
Abu Haija, M.: SS-ThP5, 42
Acharya, D.: SS2-MoM5, **3**
Adams, R.D.: SS2-MoA9, 9
Adler, H.: SS2-ThA11, 41
Adles, E.J.: SS2-FrM1, 47
Ahn, C.H.: SS1+EM-MoA4, 7
Aksoy, F.: IS+SS-ThM2, 33
Alcami, M.: SS2-ThA10, 40
Alexandrowicz, G.: SS2-WeA12, 32
Allison, W.: SS2-WeA1, 30; SS2-WeA12, 32
Al-Mahboob, A.: SS1-FrM4, 45
Aloni, S.: SS2-MoA11, 10
Altman, E.I.: SS1+EM-MoA4, 7
Andersen, J.N.: SS1+EM-MoA7, 7
Anniyev, T.: IS+SS-ThM12, 34; SS3-TuA7, **18**
Arawaka, I.: TR+SS-TuA1, 20
Artemenko, A.G.: SS1+AS+TF-ThM4, 34
Aruga, T.: SS2-WeA2, 30; SS-TuP2, 22
Arumainayagam, C.: SS1+PS+TF+AS+NS-TuA11, 16
Ashby, P.: SS-ThP16, 44
Aspnes, D.E.: SS2-FrM1, 47
Asscher, M.: SS2-TuM11, **13**; SS3-TuA10, 19; SS-TuP1, 22
Athavan, N.: SS2-MoM11, 4
Auerbach, D.J.: SS2-WeA11, **31**

— B —

Baer, M.: SS1-WeA9, 29
Bagus, P.S.: SS2-WeM12, **28**
Balaz, S.: SS1-FrM9, 47
Ballav, N.: SS2-ThM5, 36
Baricuatro, J.H.: SS2-WeM6, 27
Barry, P.: TR+SS-TuA9, 20
Bartels, L.: SS2-WeA7, **31**
Bartelt, N.C.: SS1-WeM11, 26; SS-ThP18, 44
Barth, J.V.: SS2-ThA3, **40**
Bartynski, R.A.: SS2-TuA11, 18; SS2-TuM5, 13
Baski, A.A.: SS2-TuA3, 17
Bebensee, F.: SS2-WeM6, 27
Becerra-Toledo, A.E.: SS1-WeA10, **30**
Beck, K.M.: IS+SS-ThM6, 33
Becker, C.: SS1-TuM10, 12; SS2-TuM10, 13
Beerbom, M.M.: SS1-TuM1, 11
Behm, R.J.: SS2-ThA9, 40; SS2-ThM11, 37
Bellitto, V.J.: SS1+AS+TF-ThM9, **35**
Bent, S.F.: SS1-MoM1, 1; SS1-MoM2, 1
Bertil-Bautista, L.: SS-ThP4, 42
Bermudez, V.: SS1+AS+TF-ThM3, **34**
Besenbacher, F.: SS3-TuA8, 19
Beyer, A.: SS2-ThM12, 37
Bhadj Hamouda, A.: SS1-ThA4, 38
Bhatti, A.S.: SS-TuP13, 24
Bhoj, A.: SS1-FrM8, **46**
Bhushan, B.: TR+SS-TuA11, 21
Bianco, G.V.: SS2-TuA1, 16
Bishop, S.R.: SS1+EM-MoA10, 8; SS1+EM-MoA3, 6; SS2-WeM2, 27
Blomquist, J.E.: SS1-WeA4, 29
Bluhm, H.: IS+SS-ThM1, 33; IS+SS-ThM11, 34; IS+SS-ThM2, 33; IS+SS-ThM5, 33; SS1-WeM4, 25; SS3-TuA8, 19; SS-TuP8, 23
Bogart, K.H.A.: SS3-TuA9, 19
Bonander, J.R.: SS1-WeM1, 25
Borgström, M.T.: SS1+EM-MoA7, 7
Borondics, F.: IS+SS-ThM5, **33**; SS3-TuA8, 19; SS-TuP8, 23
Bostwick, A.: SS-TuP11, 23
Brede, J.: SS-ThP8, 43
Breinlich, C.: SS2-TuM10, **13**
Breittruck, A.: SS2-ThA9, 40
Bresin, M.: SS1+PS+TF+AS+NS-TuA2, **15**
Breuer, S.: SS2-ThM2, **35**; SS2-ThM3, 36
Broach, A.L.: SS1+AS+TF-ThM10, 35

Broekmann, P.: SS2-ThM2, 35; SS2-ThM3, 36
Brown, A.S.: SS2-TuA1, 16
Brown, G.E.: IS+SS-ThM11, 34
Brown, Jr., G.: SS1-WeM4, 25
Brown, M.A.: SS1-WeM9, 26
Bruno, G.: SS2-TuA1, 16
Buck, M.: SS2-ThM6, 36
Bussmann, E.: SS1-ThA10, 39
Butcher, D.: IS+SS-ThM2, 33; SS2-MoA11, 10

— C —

Caballero, A.: IS+SS-ThM5, 33
Caldwell, J.: GR+SS-MoA3, 5
Callahan, K.: SS1-WeM9, 26
Camara, C.B.: TR+SS-TuA3, 20
Cameron, L.G.: SS3-TuA3, 18
Camillone, N.: SS2-WeM3, 27
Campbell, C.T.: SS2-WeM6, 27; SS3-TuA3, **18**
Campbell, P.M.: GR+SS-MoA3, 5
Campbell, V.L.: SS2-WeA10, 31
Capezzuto, P.: SS2-TuA1, 16
Carraro, C.: GR+SS-MoA11, 6
Carrizales, C.E.: SS-ThP9, 43
Castell, M.R.: SS2-MoM1, 2
Castner, D.G.: SS2-FrM6, 48
Cavalero, R.: GR+SS-MoA7, 5
Cerdeja, J.L.: SS1-WeM12, 26; SS2-TuM1, 12
Cerruti, M.: GR+SS-MoA11, **6**
Chabal, Y.: SS1-MoM5, 1; SS1-MoM6, 1
Chamberlin, S.E.: SS2-MoM2, **3**
Chambers, S.A.: SS1-MoM8, 2
Chang, S.: SS2-ThA8, 40; SS-ThP8, **43**
Chen, D.A.: SS2-MoA8, 9
Chen, J.-H.: GR+SS-MoA4, 5
Chen, M.S.: SS1-MoM11, 2
Chen, N.: SS2-WeA10, 31
Cheng, M.H.: SS2-ThM9, **36**; SS-ThP16, 44
Cheng, Z.: SS2-WeA7, 31
Cherkashinin, G.: SS2-ThM2, 35
Chiang, S.: SS1-ThA9, 38
Chitre, K.: SS2-TuA11, 18
Chiu, P.: TR+SS-TuA9, 20
Chiu, Y.P.: SS1-ThA11, **39**
Cho, J.: SS-ThP4, **42**
Cho, K.: SS1-MoM5, 1
Choi, B.Y.: SS1-WeM10, **26**; SS-ThP11, 43
Chopra, I.S.: SS1-MoM5, **1**; SS1-MoM6, 1
Christopher, S.: SS2-MoA3, **9**
Ciftlikli, E.Z.: SS2-TuM5, **13**
Claessens, C.: SS1-FrM2, 45
Clark, K.: SS2-ThA8, 40
Clemens, J.B.: SS1+EM-MoA3, **6**
Cohen, S.R.: TR+SS-TuA10, 21
Coker, E.N.: SS3-TuA9, 19
Colavita, P.: SS2-FrM5, 48
Collings, M.P.: SS1-WeA1, 29; SS1-WeA2, 29
Coltrin, M.E.: SS3-TuA9, 19
Conrad, M.: SS1-TuM1, 11
Creighton, J.R.: SS3-TuA9, **19**
Crommie, M.F.: SS-ThP4, 42
Cross, K.C.: SS3-TuA9, 19
Croy, J.: SS-TuP6, **23**
Cuenya, B.R.: SS2-MoA6, **9**
Cullen, W.: GR+SS-MoA4, 5

— D —

Dao, N.: SS1-MoM5, 1; SS1-MoM6, 1
David, J.M.: SS-ThP17, 44
Davila, S.: SS1-FrM6, 46
Davis, R.C.: SS2-FrM4, 48
de Jong, A.F.: SS1+PS+TF+AS+NS-TuA8, 16
de la Figuera, J.: SS2-TuM1, 12
Deodeshmukh, V.: SS1-FrM10, 47
Desai, T.V.: SS1-FrM3, **45**
Deskina, A.: SS2-MoM8, 3; SS2-WeM10, 28
Devarajan, S.P.: SS1-TuM11, 12
Devine, B.: TR+SS-TuA8, 20

Diaconescu, B.: SS2-ThA6, **40**
Diebold, U.: SS2-MoM3, **3**
Diederich, F.: SS2-ThA1, 39
Dil, H.: SS2-ThA7, 40
Dilullo, A.: SS2-ThA8, 40
Dingemans, G.: SS2-FrM2, 47
Dohnalek, Z.: SS2-MoM8, 3; SS2-WeM10, 28
Dohnálek, Z.: SS1-WeA9, 29
Doren, D.: SS2-FrM9, **48**
Du, Y.: SS2-MoM8, 3; SS2-WeM10, **28**
Dubey, M.: SS2-FrM6, **48**
Dürr, M.: SS1+PS+TF+AS+NS-TuA12, **16**; SS2-FrM8, 48
Dugerjav, O.: SS-ThP1, 42; SS-ThP2, 42
Dunin-Borkowski, R.E.: SS1+PS+TF+AS+NS-TuA7, 15
Dunn, K.A.: SS1+PS+TF+AS+NS-TuA2, 15
Dupuis, M.: SS2-MoM8, 3; SS2-WeM10, 28
Durand, A.: SS1-ThA9, 38
Duvjir, G.: SS-ThP1, 42; SS-ThP2, 42
Dvorak, S.D.: TR+SS-TuA2, 20

— E —

Ecija, D.: SS2-ThA10, 40; SS2-ThM10, 36
Eddy, Jr., C.R.: SS2-TuA2, 17
Einstein, T.: SS1-ThA4, 38
Ellis, J.: SS2-WeA1, 30; SS2-WeA12, 32
Enache, M.: SS2-ThA1, 39
Engelhard, M.H.: SS1-FrM10, 47; SS3-TuA11, 19
Engstrom, J.R.: SS1-FrM3, 45
Erdemir, A.: TR+SS-TuA12, **21**
Ermanoski, I.: SS-ThP18, **44**
Eryilmaz, O.: TR+SS-TuA12, 21
Escaño, M.C.S.: SS-TuP10, 23
Escobar, J.V.: TR+SS-TuA3, 20
Evans, J.: SS3-TuA1, 18
Evans, J.W.: SS1-ThA3, 38; SS2-WeM11, 28

— F —

Fairbrother, H.: SS1+PS+TF+AS+NS-TuA1, **15**
Fanton, M.A.: GR+SS-MoA10, **6**; GR+SS-MoA3, 5; GR+SS-MoA7, 5
Faubel, M.: SS1-WeM9, 26
Fdez-Sanz, J.: SS3-TuA1, 18
Feenstra, R.: GR+SS-MoA6, 5
Feibelman, P.J.: SS1-WeM12, 26
Fendt, L.-A.: SS2-ThA1, 39
Ferralis, N.: GR+SS-MoA11, 6
Fian, A.: SS1+EM-MoA7, 7
Fisher, P.: GR+SS-MoA6, **5**
Foussekis, M.A.: SS2-TuA3, 17
Franking, R.: SS1-MoM8, 2
Frankland, V.L.: SS1-WeA1, **29**
Frantz, E.: GR+SS-MoA7, 5
Fréchet, J.M.J.: SS-ThP4, 42
Fuhrer, M.: GR+SS-MoA4, 5
Fujikawa, Y.: SS1-FrM4, 45
Furuta, T.: SS-ThP12, **43**

— G —

Gade, L.H.: SS2-ThA7, 40
Gallego, J.M.: SS1-FrM2, 45; SS2-ThA10, 40; SS2-ThM10, 36
Galoppini, E.: SS2-TuA11, 18
Gamble, L.J.: SS2-FrM6, 48
Gann, R.D.: SS1-FrM9, **47**; SS1-TuM3, **11**
Gao, H.J.: SS2-WeA8, 31
García Flores, H.G.: SS1+AS+TF-ThM10, **35**
Garrity, K.: SS1+EM-MoA4, 7
Gartsman, K.: TR+SS-TuA10, 21
Gaskill, D.K.: GR+SS-MoA3, 5
Gassman, P.L.: SS1-FrM5, 46
Ge, S.: TR+SS-TuA11, 21
Ge, Y.: SS2-ThA11, 41
Gebhardt, C.: SS1+PS+TF+AS+NS-TuA12, 16
Gellman, A.J.: SS2-TuM9, **13**; SS2-WeM1, 26
GhezelAyagh, H.: SS1-FrM10, 47

Giangregorio, M.: SS2-TuA1, 16
 Gielis, J.J.H.: SS2-FrM2, 47
 Glaser, E.: GR+SS-MoA3, 5
 Gokce, B.: SS2-FrM1, 47
 Götzhäuser, A.: SS2-ThM12, 37
 Gorai, P.: SS2-FrM10, 49
 Gorb, L.G.: SS1+AS+TF+ThM4, 34
 Gorham, J.: SS1+PS+TF+AS+NS-TuA1, 15
 Gottfried, J.M.: SS2-WeM6, 27
 Grabow, L.: SS3-TuA3, 18
 Graciani, J.: SS1-TuM9, 11; SS3-TuA1, 18
 Grass, M.: IS+SS-ThM2, 33; SS2-MoA11, 10
 Grassian, V.: SS1-WeM5, 25
 Grimm, R.L.: SS2-ThM9, 36; SS-ThP16, 44
 Groß, A.: SS2-ThA9, 40
 Gross, E.: SS3-TuA10, 19; SS-TuP1, 22
 Grundmeier, G.: SS2-TuA10, 17
 Gschwender, L.: SS1-WeA3, 29
 Gu, G.D.: SS1-TuM3, 11
 Gundogdu, K.: SS2-FrM1, 47
 Guo, Q.: SS1-FrM1, 45
 Gutmann, S.: SS1-TuM1, 11

— H —

Hagen, K.: SS1+PS+TF+AS+NS-TuA1, 15;
 SS1+PS+TF+AS+NS-TuA7, 15
 Hakanoglu, C.: SS1-TuM11, 12
 Ham, H.: SS2-MoA2, 8; SS2-TuM12, 14
 Hamada, I.: SS2-WeA2, 30; SS-TuP2, 22
 Hamers, R.J.: SS1-MoM8, 2; SS2-FrM5, 48; SS2-
 ThM4, 36
 Han, Y.: SS1-ThA3, 38
 Hansen, T.W.: SS1+PS+TF+AS+NS-TuA7, 15
 Hatta, S.: SS2-WeA2, 30; SS-TuP2, 22
 Hedgeland, H.J.: SS2-WeA1, 30; SS2-WeA12, 32
 Heinrich, H.: SS-TuP6, 23
 Heller, E.J.: SS3-TuA9, 19
 Hemminger, J.C.: IS+SS-ThM3, 33; SS1-WeM9,
 26; SS2-ThM9, 36; SS-ThP16, 44
 Henderson, M.A.: IS+SS-ThM6, 33; SS2-MoM9, 3
 Herranz, M.A.: SS2-ThA10, 40
 Herranz, T.: SS2-TuM1, 12
 Hersam, M.C.: SS-TuP5, 23
 Hill, F.C.: SS1+AS+TF+ThM4, 34
 Hilner, E.: SS1+EM-MoA7, 7
 Hinch, B.J.: SS2-TuM5, 13
 Hinkle, C.L.: SS1+EM-MoA1, 6
 Hinze, P.: SS2-ThM12, 37
 Hipps, K.W.: SS-ThP9, 43
 Hird, J.: TR+SS-TuA3, 20
 Hirschmugl, C.J.: SS2-MoM2, 3
 Hjort, M.: SS1+EM-MoA7, 7
 Hla, S.-W.: SS2-ThA8, 40
 Ho, W.: SS2-WeA8, 31; SS2-WeA9, 31
 Höfer, U.: SS2-FrM8, 48
 Hoffmann, G.: SS2-ThA8, 40; SS-ThP10, 43; SS-
 ThP8, 43
 Holsclaw, B.: SS2-WeM1, 26
 Hong, S.: SS1-FrM3, 45
 Hosobuchi, E.: TR+SS-TuA1, 20
 Hoster, H.E.: SS2-ThA9, 40; SS2-ThM11, 37
 Hrbek, J.: SS1-TuM9, 11; SS3-TuA1, 18
 Hsieh, J.H.: SS-TuP19, 24
 Hu, Q.: SS1-FrM5, 46
 Hu, X.: SS2-TuM6, 13
 Huan, Q.: SS2-WeA8, 31
 Huang, B.C.: SS1-ThA11, 39
 Huang, M.: SS1-MoM5, 1
 Huang, P.: SS1-WeA12, 30
 Huemann, S.: SS2-ThM3, 36
 Hughes, K.J.: SS1-FrM3, 45
 Hughes, Z.: GR+SS-MoA7, 5
 Hunger, R.: SS2-ThM3, 36
 Hussein, Z.: IS+SS-ThM2, 33
 Hwang, G.: SS2-MoA2, 8; SS2-TuM12, 14

— I —

Ismail-Beigi, S.: SS1+EM-MoA4, 7
 Isobe, T.: SS-ThP12, 43

— J —

Jang, C.: GR+SS-MoA4, 5
 Jardine, A.P.: SS2-WeA1, 30; SS2-WeA12, 32
 Jazdzzyk, M.: SS2-ThA6, 40
 Jenks, C.J.: SS2-WeM11, 28
 Jernigan, G.G.: GR+SS-MoA3, 5
 Ji, Y.: SS2-WeA11, 31
 Jiang, P.: IS+SS-ThM5, 33; SS3-TuA8, 19; SS-
 TuP8, 23
 Jiang, W.: SS3-TuA11, 19
 Jiang, Y.J.: SS2-WeA9, 31
 Jing, D.: SS1-ThA3, 38
 Jung, J.: SS1-WeM3, 25
 Jung, T.A.: SS2-ThA1, 39; SS2-ThA7, 40

— K —

Kachian, J.S.: SS1-MoM1, 1
 Kaizu, M.: SS2-WeA2, 30; SS-TuP2, 22
 Kalyanaraman, V.: SS-ThP5, 42
 Kameshima, Y.: SS-ThP12, 43
 Kampen, T.: SS-TuP7, 23
 Kaplan-Ashiri, I.: TR+SS-TuA10, 21
 Kasai, H.: SS-TuP10, 23
 Kasemo, B.H.: SS2-MoA1, 8
 Katalinic, S.: SS2-TuA11, 18
 Kawai, M.: SS1-TuM4, 11; SS1-WeM3, 25; SS2-
 WeM4, 27; SS-ThP13, 43
 Kay, B.: SS1-WeA9, 29; SS-ThP7, 42
 Kaya, S.: IS+SS-ThM11, 34; SS1-WeM4, 25; SS3-
 TuA7, 18
 Kedzierski, J.: GR+SS-MoA6, 5
 Kelley, J.M.: SS1+AS+TF+ThM9, 35
 Kellogg, G.: SS-ThP18, 44
 Kendelewicz, T.: IS+SS-ThM11, 34; SS1-WeM4,
 25
 Kern, K.: SS2-ThA10, 40
 Kessels, W.M.M.: SS1+PS+TF+AS+NS-TuA8,
 16; SS2-FrM2, 47
 Khajetoorians, A.: SS1-ThA2, 38; SS2-TuM2, 12
 Kholod, Y.I.: SS1+AS+TF+ThM4, 34
 Kienzle, D.M.: SS1-WeA10, 30
 Kim, B.I.: SS1-WeM1, 25
 Kim, E.J.: SS1-WeM1, 25
 Kim, H.: SS1-MoM8, 2; SS-ThP1, 42; SS-ThP2,
 42
 Kim, H.-Y.: SS2-TuA2, 17
 Kim, J.: SS2-TuA2, 17; SS2-TuM2, 12
 Kim, J.D.: SS1-ThA2, 38
 Kim, T.H.: SS2-TuA1, 16
 Kim, Y.: SS1-TuM4, 11; SS1-WeM3, 25; SS2-
 WeM4, 27
 Kim, Y.J.: SS3-TuA11, 19
 Kim, Y.-S.: SS-TuP11, 23
 Kimmel, G.A.: SS1-WeA9, 29; SS2-MoM6, 3;
 SS2-MoM8, 3
 Kinder, R.: SS1-FrM8, 46
 Kirk, W.P.: SS1-MoM5, 1; SS1-MoM6, 1
 Kitajima, T.: SS1-FrM7, 46
 Klein, T.M.: SS-ThP3, 42
 Ko, C.: SS1-TuM5, 11
 Kober, M.: SS-TuP8, 23
 Köber, M.: IS+SS-ThM5, 33; SS3-TuA8, 19
 Kobiela, T.: SS2-TuM10, 13
 Koehler, S.P.: SS2-WeA11, 31
 Koel, B.: IS+SS-ThM1, 33
 Koh, S.: SS3-TuA7, 18
 Kompa, K.: SS1+PS+TF+AS+NS-TuA12, 16
 Kondratenko, Y.: SS2-FrM10, 49
 Koo, J.: SS2-FrM3, 47
 Kothnur, P.: SS1-FrM8, 46
 Kratzer, M.C.: SS-TuP13, 24
 Krupczak, E.: SS1+PS+TF+AS+NS-TuA11, 16
 Kuchibhatla, S.V.N.T.: SS1-FrM10, 47; SS3-
 TuA11, 19
 Kuck, S.: SS2-ThA8, 40; SS-ThP10, 43; SS-ThP8,
 43
 Kuehnle, A.: SS-TuP18, 24
 Künzel, D.: SS2-ThA9, 40
 Kumagai, T.: SS2-WeA2, 30; SS-TuP2, 22

Kummel, A.C.: SS1+EM-MoA10, 8; SS1+EM-
 MoA3, 6; SS1+EM-MoA6, 7; SS2-WeM2, 27
 Kunikata, S.: SS-TuP10, 23
 Kurtz, R.L.: SS2-MoM10, 4
 Kuzmin, V.E.: SS1+AS+TF+ThM4, 34
 Kwak, J.: SS1-TuM6, 11

— L —

LaBella, M.: GR+SS-MoA10, 6; GR+SS-MoA7, 5
 Lake, R.E.: SS-ThP6, 42
 Lallo, J.: SS2-TuM5, 13
 Landis, E.C.: SS1-MoM8, 2; SS2-ThM4, 36
 Langhammer, C.M.: SS2-MoA1, 8
 Larsson, E.M.: SS2-MoA1, 8
 Laskin, J.: SS1-FrM5, 46
 Lau, S.: SS1+PS+TF+AS+NS-TuA11, 16
 Le Moal, S.: SS1-TuM10, 12
 Lea, A.S.: SS1-FrM10, 47
 Lee, E.: SS2-WeA12, 32
 Lee, E.Y.-M.: SS2-TuM5, 13
 Lee, G.: SS2-FrM3, 47
 Lee, G.Y.: TR+SS-TuA2, 20
 Lee, J.S.: SS1+EM-MoA10, 8
 Lee, M.: SS1-TuM12, 12
 Lee, S.: SS1+EM-MoA6, 7
 Lee, W.: SS2-FrM3, 47
 Leszczynski, J.R.: SS1+AS+TF+ThM1, 34;
 SS1+AS+TF+ThM4, 34
 Leung, K.T.: SS2-FrM7, 48
 Levy, N.: SS-ThP4, 42
 Lewis, T.L.: SS1-WeM9, 26
 Li, H.: SS-ThP1, 42; SS-ThP2, 42
 Li, K.: SS-ThP3, 42
 Li, N.: SS-ThP3, 42
 Lichtenstein, L.: SS-ThP10, 43
 Linford, M.R.: SS2-FrM4, 48
 Linic, S.: SS2-MoA3, 9
 Liu, D.-J.: SS2-WeM11, 28
 Liu, G.: IS+SS-ThM1, 33
 Liu, P.J.: SS1-TuM9, 11; SS2-WeM3, 27; SS3-
 TuA1, 18; SS3-TuA4, 18
 Liu, Z.: IS+SS-ThM2, 33; SS-ThP16, 44; SS-
 TuP8, 23
 Lobo-Checa, J.: SS2-ThA7, 40
 Loscutoff, P.W.: SS1-MoM2, 1
 Losurdo, M.: SS2-TuA1, 16
 Lukanov, B.: SS1+EM-MoA4, 7
 Lukaszew, R.A.: SS1-ThA6, 38
 Lundgren, E.: SS1+EM-MoA7, 7
 Luo, M.: SS2-WeA7, 31
 Luxmi, L.: GR+SS-MoA6, 5
 Lyubinetzky, I.: SS2-MoM8, 3; SS2-WeM10, 28

— M —

Ma, S.J.: SS3-TuA1, 18
 Maboudian, R.: GR+SS-MoA11, 6
 Mackus, A.J.M.: SS1+PS+TF+AS+NS-TuA8, 16
 Madey, T.: SS1+PS+TF+AS+NS-TuA1, 15
 Maekawa, H.: SS-TuP10, 23
 Mähl, S.: SS-TuP7, 23
 Maier, S.: SS1-WeA11, 30; SS1-WeM12, 26; SS2-
 WeM5, 27
 Makabe, T.: SS1-FrM7, 46
 Margarella, A.: SS-ThP16, 44
 Markovic, N.: SS-TuP11, 23
 Marks, L.D.: SS1-WeA10, 30
 Martin, F.: SS2-ThA10, 40
 Martin, N.: SS2-ThA10, 40; SS2-ThM10, 36
 Mastro, M.A.: SS2-TuA2, 17
 Matena, M.: SS2-ThA7, 40
 Matthiesen, J.: SS1-WeA9, 29; SS-ThP7, 42
 Mavrikakis, M.: SS3-TuA3, 18
 Mayer, J.: SS2-ThM12, 37
 Mbuga, F.: IS+SS-ThM11, 34
 McCarty, K.F.: SS2-TuM1, 12
 McCoustra, M.R.S.: SS1-WeA1, 29; SS1-WeA2,
 29
 McGaughey, A.: SS1-TuM12, 12
 McIntire, T.: SS2-ThM9, 36; SS-ThP16, 44
 Medina, A.: SS1-FrM2, 45

- Megahed, M.: SS1-FrM8, 46
Melitz, W.: SS1+EM-MoA6, 7
Mette, G.: SS2-FrM8, 48
Meyer, R.J.: SS2-MoA9, 9; SS2-TuM6, 13
Meyer, T.: SS2-ThM2, 35
Mikkelsen, A.: SS1+EM-MoA7, 7; SS1+EM-MoA8, 7
Miller, D.J.: IS+SS-ThM12, 34
Miller, G.: SS2-ThA6, 40
Miller, J.B.: SS2-TuM9, 13
Milojevic, M.: SS1+EM-MoA1, 6
Minter, A.: SS1-TuM11, 12
Miranda, R.: SS1-FrM2, 45; SS2-ThA10, 40; SS2-ThM10, 36
Miura, T.: TR+SS-TuA1, 20
Moore, D.P.: SS1+AS+TF-ThM10, 35
Moors, M.: SS1-TuM10, 12; SS2-TuM10, 13
Morad, J.: SS1-ThA9, 38
Morikawa, Y.: SS2-WeA2, 30; SS-TuP2, 22
Mostafa, S.: SS-TuP6, 23
Motobayashi, K.: SS1-WeM3, 25
Mudiyanselage, K.: SS1-MoM10, 2
Mulders, H.J.L.: SS1+PS+TF+AS+NS-TuA8, 16
Mullet, C.: SS1-ThA9, 38
Mullins, C.B.: SS2-TuM3, 13
Mun, B.S.: IS+SS-ThM2, 33; SS-TuP11, 23
Mundy, C.: SS1-WeA9, 29
Muratov, E.N.: SS1+AS+TF-ThM4, 34
Myneni, S.C.B.: IS+SS-ThM9, 33
Mysak, E.: SS1-WeM4, 25
- N —
Naboka, M.: SS-TuP18, 24
Nachimuthu, P.: IS+SS-ThM6, 33; SS2-MoM11, 4; SS3-TuA11, 19
Nadesalingam, M.P.: SS1-MoM5, 1; SS1-MoM6, 1
Naitabdi, A.: SS2-MoA10, 10
Nakajima, A.: SS-ThP12, 43; SS-ThP14, 44; SS-ThP15, 44
Nakanishi, H.: SS-TuP10, 23
Nakano, T.: SS1-FrM7, 46
Nandasiri, M.: SS3-TuA11, 19
Nasim, F.: SS-TuP13, 24
Näslund, L.-Å.: IS+SS-ThM12, 34
Nefedov, A.: SS-TuP18, 24
Nelsen, E.: SS2-FrM4, 48
Neugebauer, J.: SS2-TuA10, 17
Newberg, J.: IS+SS-ThM11, 34; SS1-WeM4, 25
Nguyen, T.Q.: SS-TuP10, 23
Nie, S.: SS1-WeM11, 26
Nilsson, A.: IS+SS-ThM11, 34; IS+SS-ThM12, 34; SS1-WeM4, 25; SS3-TuA7, 18
Nimmrich, M.: SS-TuP18, 24
Nolph, C.A.: SS1+EM-MoA11, 8
Nottbohm, Ch.T.: SS2-ThM12, 37
- O —
Ogasawara, H.: IS+SS-ThM11, 34; IS+SS-ThM12, 34; SS3-TuA7, 18
Ogitsu, T.: SS-ThP20, 44
Oh, D.: SS1+PS+TF+AS+NS-TuA3, 15
Okada, K.: SS-ThP12, 43
Okada, T.: SS2-WeM4, 27
Okuyama, H.: SS2-WeA2, 30; SS-TuP2, 22
Ono, L.K.: SS2-MoA10, 10; SS-TuP6, 23
Orlando, T.M.: SS1+PS+TF+AS+NS-TuA3, 15
Osgood, R.M.: SS2-WeM9, 28
Osumi, K.: SS-TuP10, 23
Otero, R.: SS1-FrM2, 45; SS2-ThA10, 40; SS2-ThM10, 36
- P —
Park, J.B.: SS1-TuM9, 11; SS3-TuA1, 18
Peden, C.: SS1-TuM6, 11
Perrine, K.A.: SS-TuP4, 22
Perry, S.S.: TR+SS-TuA7, 20
Petrik, N.G.: SS1-WeA9, 29; SS2-MoM6, 3; SS2-MoM8, 3
Pham, D.-T.: SS2-ThM2, 35; SS2-ThM3, 36
Phillpot, S.R.: TR+SS-TuA7, 20; TR+SS-TuA8, 20; TR+SS-TuA9, 20
- Piercy, P.: SS-ThP17, 44
Pimpinelli, A.: SS1-ThA4, 38
Pohl, D.: SS-ThP17, 44
Pohl, K.: SS2-ThA6, 40
Pollmann, J.: SS2-TuA7, 17
Poon, H.C.: SS2-MoM2, 3
Porsgaard, S.: IS+SS-ThM5, 33; SS1-WeM4, 25; SS3-TuA8, 19; SS-TuP8, 23
Potapenko, D.V.: SS2-WeM9, 28
Poulsen, D.: SS-ThP4, 42
Priyadarshini, D.: SS2-TuM9, 13
Puerta, J.M.: SS2-TuM1, 12
Pugmire, D.L.: SS1+AS+TF-ThM10, 35
Putnam, S.: SS1-WeA3, 29
Putterman, S.: TR+SS-TuA3, 20
- Q —
Qin, S.Y.: SS1-ThA2, 38
Qiu, H.: SS1-MoM9, 2
- R —
Rahe, P.: SS-TuP18, 24
Ramanathan, S.: SS1-TuM5, 11
Randall, J.: SS1-MoM5, 1; SS1-MoM6, 1
Rangan, S.: SS2-TuA11, 18; SS2-TuM5, 13
Ratliff, J.S.: SS2-MoA8, 9
Ratner, D.: SS2-FrM6, 48
Ray, M.P.: SS-ThP6, 42
Reiner, J.: SS1+EM-MoA4, 7
Reinke, P.: SS1+EM-MoA11, 8; SS1-TuM5, 11
Ren, J.: SS1-TuM12, 12
Renzas, J.R.: SS2-MoA11, 10
Reshchikov, M.A.: SS2-TuA3, 17
Reutt-Robey, J.: SS2-ThA2, 39
Reynolds, N.P.: SS2-ThA1, 39
Roberts, C.C.: SS2-MoA8, 9
Robey, S.: SS2-ThA2, 39
Robinson, J.A.: GR+SS-MoA10, 6; GR+SS-MoA3, 5; GR+SS-MoA7, 5
Rochford, J.: SS2-TuA11, 18
Rodriguez, J.A.: SS1-TuM9, 11; SS3-TuA1, 18
Rodriguez-Reyes, J.C.F.: SS-TuP3, 22
Roldan Cuenya, B.: SS2-MoA10, 10; SS-TuP6, 23
Roos, M.: SS2-ThA9, 40; SS2-ThM11, 37
Rosenberg, R.A.: SS-ThP5, 42
Rosenberg, S.: SS1+PS+TF+AS+NS-TuA1, 15
Ross, P.N.: SS-TuP11, 23
Rotenberg, E.: GR+SS-MoA8, 6; SS-TuP11, 23
Rowntree, P.A.: SS1+PS+TF+AS+NS-TuA9, 16
Russel, S.: SS2-WeM11, 28
Rutten, F.J.M.: SS1-WeA2, 29
Ryan, P.J.: SS-ThP5, 42
- S —
Sadowski, J.T.: SS1-FrM4, 45
Safarowsky, C.: SS2-ThM3, 36
Sakai, M.: SS-ThP12, 43; SS-ThP14, 44; SS-ThP15, 44
Sakurai, T.: SS1-FrM4, 45
Saldin, D.K.: SS2-MoM2, 3
Salmeron, M.: IS+SS-ThM5, 33; SS1-WeA11, 30; SS1-WeM10, 26; SS1-WeM12, 26; SS1-WeM4, 25; SS2-MoA11, 10; SS2-WeM5, 27; SS3-TuA8, 19; SS-ThP11, 43; SS-TuP8, 23
Samuelson, L.: SS1+EM-MoA7, 7
Santos, B.: SS2-TuM1, 12
Sathiyarayanan, R.: SS1-ThA4, 38
Sawyer, G.: TR+SS-TuA7, 20
Schaff, O.: SS-TuP7, 23
Schilp, S.: SS2-ThM5, 36
Schlaad, H.: SS2-FrM4, 48
Schlaf, R.: SS1-TuM1, 11
Schroder, H.: SS1+PS+TF+AS+NS-TuA12, 16
Schwalb, C.H.: SS2-FrM8, 48
Schwegler, E.: SS1-WeA12, 30; SS-ThP20, 44
Schwöbel, J.: SS-ThP8, 43
Seebauer, E.G.: SS2-FrM10, 49; SS-TuP13, 24
Seifert, G.: TR+SS-TuA10, 21
Seitz, O.: SS1-MoM5, 1
Senanayake, S.: SS1-TuM9, 11
Seo, J.M.: SS-ThP1, 42; SS-ThP2, 42
- Shah, K.: SS1-FrM8, 46
Shan, T.R.: TR+SS-TuA8, 20
Sharp, J.C.: SS2-WeM6, 27
Shen, C.: SS2-ThM6, 36
Shen, C.Y.: SS1-ThA11, 39
Shen, J.: SS1+EM-MoA6, 7
Shen, M.: SS2-WeM11, 28
Shepperd, K.: SS1+PS+TF+AS+NS-TuA3, 15
Shi, Y.: SS1-WeM10, 26; SS-ThP11, 43
Shih, C.K.: SS1-ThA2, 38; SS2-TuM2, 12
Shim, H.: SS2-FrM3, 47
Shimizu, T.K.: SS1-TuM4, 11
Shin, H.-J.: SS1-WeM3, 25
Shutthanandan, V.: SS1-FrM10, 47; SS2-MoM11, 4; SS3-TuA11, 19
Shyur, Y.: SS1+PS+TF+AS+NS-TuA11, 16
Silien, C.: SS2-ThM6, 36
Simov, K.R.: SS1+EM-MoA11, 8
Singer, I.L.: TR+SS-TuA2, 20
Singh, P.: SS1-FrM10, 47
Sinnott, S.B.: TR+SS-TuA7, 20; TR+SS-TuA8, 20; TR+SS-TuA9, 20
Smith, R.S.: SS1-WeA9, 29; SS-ThP7, 42
Snyder, D.: GR+SS-MoA7, 5
Sokolov, D.: SS1+PS+TF+AS+NS-TuA3, 15
Sologubenko, A.: SS2-ThM12, 37
Somorjai, G.A.: IS+SS-ThM2, 33; SS2-MoA11, 10
Sonnet, A.M.: SS1+EM-MoA1, 6
Sorensen, D.N.: SS1+AS+TF-ThM9, 35
Sosolik, C.E.: SS-ThP6, 42
Sprunger, P.: SS2-MoM10, 4
Squires, K.H.: SS1-MoM1, 1
Srivastava, N.: GR+SS-MoA6, 5
Stacchiola, D.J.: SS1-TuM9, 11; SS3-TuA1, 18
Stamenkovic, V.: SS-TuP11, 23
Starr, D.: SS1-WeM4, 25
Stass, I.: SS1-WeA11, 30; SS1-WeM12, 26; SS2-WeM5, 27
Steinrueck, H.-P.: SS2-WeM6, 27
Stephens, J.: SS2-TuM12, 14
Stöhr, M.: SS2-ThA1, 39; SS2-ThA7, 40
Stosch, R.: SS2-ThM12, 37
Strasser, P.: SS3-TuA7, 18
Streifer, J.: SS2-FrM5, 48
Strongin, D.R.: SS1-WeA7, 29
Stroschio, J.A.: GR+SS-MoA1, 5
Sun, D.: SS2-WeA7, 31
Sun, Y.: GR+SS-MoA6, 5
Sutter, P.W.: SS2-MoM5, 3
Swartzentruber, B.S.: SS1-ThA10, 39
Sykes, C.E.: SS2-WeA3, 31
Szanyi, J.: SS1-MoM10, 2; SS1-TuM6, 11; SS3-TuA11, 19
- T —
Taing, J.: SS-ThP16, 44
Tait, S.L.: SS2-ThA10, 40; SS2-ThA11, 41
Takami, T.: SS-ThP9, 43
Tang, L.: SS1-FrM1, 45
Tang, W.: TR+SS-TuA11, 21
Tao, F.: SS2-MoA11, 10
Tashiro, Y.: SS-TuP10, 23
Tedesco, J.L.: GR+SS-MoA3, 5
Tenne, R.: TR+SS-TuA10, 21
Tenney, S.A.: SS2-MoA8, 9
Tepljakov, A.V.: SS1-MoM3, 1; SS-TuP3, 22; SS-TuP4, 22
Terlinden, N.M.: SS2-FrM2, 47
Thevuthasan, S.: IS+SS-ThM6, 33; SS1-FrM10, 47; SS2-MoM11, 4; SS3-TuA11, 19
Thiel, P.A.: SS1-ThA3, 38; SS2-WeM11, 28
Thissen, A.: SS-TuP7, 23
Thorpe, R.: SS2-TuA11, 18
Thrower, J.D.: SS1-WeA2, 29
Thürmer, K.: SS1-WeM11, 26
Timm, R.: SS1+EM-MoA7, 7
Tischler, J.G.: GR+SS-MoA3, 5
Tobias, D.: SS1-WeM9, 26
Todorova, M.: SS2-TuA10, 17
Tomanek, D.: SS2-ThA6, 40

Tomsic, A.: SS1+PS+TF+AS+NS-TuA12, 16
 Toney, M.: SS3-TuA7, 18
 Torres, T.: SS1-FrM2, 45
 Tran, N.: SS2-WeM2, 27
 Tran, T.: SS1-WeM1, 25
 Trelka, M.: SS1-FrM2, **45**; SS2-ThA10, 40; SS2-ThM10, 36
 Trenary, M.: SS2-MoA9, 9; SS2-TuM6, 13; SS2-WeM4, 27
 Tripp, C.P.: SS1+AS+TF-ThM5, **35**
 Trufan, E.: SS2-MoA9, 9
 Trumbull, K.: GR+SS-MoA10, 6; GR+SS-MoA7, 5
 Tseng, C.C.: SS-TuP19, **24**
 Tseng, T.-C.: SS2-ThA10, 40
 Tskipuri, L.: SS2-TuM5, 13
 Tsukada, M.: SS1-WeM2, **25**
 Tsung, C.: SS2-MoA11, 10
 Turchanin, A.: SS2-ThM12, **37**
 — **U** —
 Ueno, S.: TR+SS-TuA1, 20
 Uhl, A.: SS2-MoA9, 9
 Unal, B.: SS1-ThA3, 38
 Urban, C.: SS1-FrM2, 45; SS2-ThA10, 40; SS2-ThM10, **36**
 Utz, A.L.: SS2-WeA10, **31**
 Uvdal, P.E.: SS1-WeA4, **29**
 — **V** —
 Valtiner, M.: SS2-TuA10, **17**
 van de Sanden, M.C.M.: SS1+PS+TF+AS+NS-TuA8, 16; SS2-FrM2, 47
 van Dorp, W.F.: SS1+PS+TF+AS+NS-TuA1, 15; SS1+PS+TF+AS+NS-TuA7, **15**
 Verbeck, G.F.: SS1-FrM6, **46**
 Verlaan, V.: SS2-FrM2, 47
 Veyan, J.-F.: SS1-MoM5, 1; SS1-MoM6, 1
 Vogel, E.M.: SS1+EM-MoA1, 6
 — **W** —
 Wagner, H.D.: TR+SS-TuA10, 21
 Wagner, J.B.: SS1+PS+TF+AS+NS-TuA7, 15

Wahl, K.J.: TR+SS-TuA2, **20**
 Wahl, M.: SS2-ThA7, 40
 Waldmann, T.: SS2-ThA9, **40**; SS2-ThM11, 37
 Walker, F.J.: SS1+EM-MoA4, 7
 Wallace, R.M.: SS1+EM-MoA1, 6; SS1-MoM5, 1; SS1-MoM6, 1
 Wan, H.L.: SS1-MoM11, 2
 Wandelt, K.: SS1-TuM10, 12; SS2-ThM2, 35; SS2-ThM3, **36**; SS2-TuM10, 13
 Wang, F.: SS2-MoM10, 4
 Wang, J.: SS1+PS+TF+AS+NS-TuA11, 16
 Wang, P.: SS1-FrM5, 46
 Wang, Q.H.: SS-TuP5, **23**
 Wang, X.: SS1-MoM11, 2; SS2-FrM5, **48**
 Wang, Y.: SS1-MoM9, **2**
 Ward, D.J.: SS2-WeA1, **30**
 Watanabe, T.: SS-ThP15, 44
 Weaver, J.F.: SS1-TuM11, **12**
 Wei, Y.: SS2-ThA2, **39**
 Weidner, T.: SS2-FrM6, 48
 Weiland, B.E.: GR+SS-MoA10, 6
 Weimann, T.: SS2-ThM12, 37
 Wen, J.: SS1-TuM3, 11
 Wendt, S.: SS3-TuA8, 19
 Wetherington, M.: GR+SS-MoA7, 5
 White, M.: SS2-WeM3, 27; SS3-TuA4, 18
 Wickard, T.: SS2-FrM4, 48
 Wieckowski, A.: SS2-WeM12, 28
 Wiesendanger, R.: SS2-ThA8, 40; SS-ThP10, 43; SS-ThP8, 43
 Williams, E.: GR+SS-MoA4, 5
 Winter, B.: SS1-WeM9, 26
 Wintjes, N.: SS2-ThA1, 39
 Wnuk, J.: SS1+PS+TF+AS+NS-TuA1, 15
 Wodtke, A.M.: SS2-WeA11, 31
 Woell, Ch.: SS-TuP18, 24
 Wolak, M.: SS1-TuM1, 11
 Wolf, S.: SS1-TuM5, 11
 Woll, A.R.: SS1-FrM3, 45
 Wöll, Ch.: SS1-MoM9, 2; SS2-WeM12, 28
 Wolter, S.D.: SS2-TuA1, 16
 Womack, F.: SS2-MoM10, 4

Wong, K.T.: SS1-MoM2, 1
 Wood, B.: SS-ThP20, **44**
 Wu, C.: SS2-MoM1, **2**
 Wu, R.Q.: SS1-TuM3, 11
 Wu, W.: SS-TuP19, 24
 — **X** —
 Xu, B.: SS2-ThM1, **35**
 Xu, Z.: SS1-TuM3, 11
 — **Y** —
 Yamada, T.: SS-ThP13, **43**
 Yamamoto, S.: SS1-WeM4, 25
 Yang, F.: SS1-TuM9, **11**
 Yang, J.C.: SS1-TuM12, 12
 Yang, L.: SS2-FrM9, 48
 Yang, T.: SS2-ThA6, 40
 Yang, W.: SS2-ThA10, 40
 Yang, Y.: SS2-WeM3, 27; SS3-TuA4, **18**
 Yarmoff, J.A.: SS1-FrM9, 47; SS1-TuM3, 11
 Yi, C.W.: SS1-MoM10, 2
 Yin, W.: SS1-TuM5, **11**
 Yoshida, N.: SS-ThP15, **44**
 Yu, S.: SS2-FrM3, 47
 Yu, Z.Q.: IS+SS-ThM6, 33; SS3-TuA11, **19**
 — **Z** —
 Zakharov, A.A.: SS1+EM-MoA7, 7
 Zegenhagen, J.: SS2-ThA7, 40
 Zehr, R.T.: SS2-MoM9, **3**
 Zhang, X.: SS1-FrM1, 45; SS2-ThM12, 37
 Zhang, Y.: SS2-MoA11, 10
 Zhang, Z.: SS2-MoM10, 4; SS2-MoM8, 3; SS2-WeM10, 28
 Zhang, Z.Y.: SS1-ThA2, 38; SS2-TuM2, 12
 Zhao, X.: TR+SS-TuA7, 20
 Zharnikov, M.: SS2-ThM5, 36
 Zhou, J.: SS1-ThA8, **38**; SS2-WeM3, **27**
 Zhou, Y.: SS1-ThA8, 38
 Zhu, W.G.: SS1-ThA2, 38; SS2-TuM2, 12
 Zhu, Z.: IS+SS-ThM6, 33; SS1-FrM10, 47
 Zoric, I.L.: SS2-MoA1, **8**