Surface Science

Room: 608 - Session SS1-MoM

Catalysis on Clusters and Nanoparticles

Moderator: M. Mavrikakis, University of Wisconsin - Madison

8:00am **SS1-MoM1 Platinum Nanoparticle Shape and Stabilizing Agent Effects on Catalysis**, ***K.M. Bratlie***, *H. Lee, P. Yang, K. Komvopoulos, G.A. Somorjai*, University of California, Berkeley

Our goal is to understand the behavior of real catalyst systems on a molecular level. To accomplish this task, a model system of capped platinum nanoparticles on a silica substrate is used. The nanoparticles exhibit a narrow size distribution and well defined shape. We were able to monitor two different shapes: cubes, comprised of {100} facets, and cuboctahedra, made of {111} and {100} facets. We were also able to investigate the influence of the capping agent on the catalytic activity of the particles. Kinetic studies of benzene hydrogenation on platinum nanoparticles over a range of temperatures (310 - 400 K) were used to relate nanoparticles to single crystals. In this manner, we uncovered implications for reaction mechanisms nanoparticle surfaces identical to analogous single crystal faces.

8:20am **SS1-MoM2 Catalytic Properties of Pt Nanoparticles on HOPG**, ***J. Nakamura***, *K. Izumi, Y. Iwasaki, T. Kondo*, University of Tsukuba, Japan

Reduction in Pt usage is one of the key requirements for the commercialization of polymer electrolyte fuel cells (PEFCs) for use in everyday life, because of its high price and limited availability, and the difficulty of finding suitable substitutes. We have reported that use of carbon nanotube (CNT) as an electrode material results in high performance with low loading of Pt. That is, the electric power of 12 wt% Pt/CNT was found to be higher than that of 29wt% Pt/carbon black. Moreover, we have observed that RuPt/CNT catalysts show higher tolerance for CO poisoning compared to RuPt/carbon black(CB) catalysts. We have thus found superior performance of CNT as a support material. The CNT used is thicker tubes with diameter of 50-80 nm compared to single wall CNT (0.7-1.5 nm). The diameter of catalyst particles ranges from 2 to 8 nm. The use of thick CNTs in PEFC is very promising because the price is going down recently. Why does CNT show good performance as a support material? There are several physical and chemical reasons. Here, we emphasize the chemical aspect of the interface between catalysts and carbon electrode. That is, difference between CNT and generally used carbon black (CB) is the surface of carbon, at which catalyst particles are attached and electron flows. The surface of thick CNT can be regarded as basal plane of graphite, while the surface of CB is composed of edges of graphene sheets. We thus use a model system of metal catalysts/HOPG (Highly oriented pyrolytic graphite). STM observation shows that Pt particles are attached like two dimension islands on HOPG instead of spherical particles. XPS measurements show that Pt 4f core level is shifted to higher energy compared to bulk Pt. The 2-d Pt particles on HOPG show very high catalytic activity for H2-D2 exchange reaction at high pressures (24 Torr). However, the catalytic activity is reduced by a factor of 30-50 upon heating above 320 K in the presence of hydrogen although no decrease in the amount of Pt is observed by the heating. This is consistent with lower peak temperature shift in TPD of H2 from Pt on HOPG. The change in the catalytic properties of 2-d Pt particles can be ascribed to electronic modification due to a lattice strain of 2-d Pt islands on HOPG. This explains the support effect of carbon supported fuel cell catalysts, that is, Pt/CNT described above.

8:40am **SS1-MoM3 Environmental Effects on Morphology of Oxide Supported Gold Nanoparticles**, ***S. Shaikhutdinov***, Fritz-Haber Institute, Germany

Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. In this paper, the morphology of Au particles deposited on thin FeO(111) and CeO2(111) films at elevated (up to 10 mbar) pressures of H2, CO, O2 and CO+O2 has been examined using in situ STM at room temperature. The Au particles are found to be fairly stable in oxygen and hydrogen environments. However, in CO+O2 (and CO) atmospheres, the destabilization of Au particles located at the step edges occurs leading to the formation of mobile Au species, which migrate across the oxide surface. General problems encountered with high-pressure STM studies will be also discussed, in particular trace impurities of the gas feedstock may play a big role in system behaviour and data interpretation.

9:00am **SS1-MoM4 The Growth and Characterization of Bimetallic Nanoclusters on Oxide Surfaces: Au-Pt on TiO_2(110)**, ***J.B. Park***, *D.A. Chen*, University of South Carolina

Gold (Au) nanoclusters deposited on TiO2 supports have been shown to be excellent catalysts for various oxidation reactions such as propylene epoxidation and CO oxidation. The size of the nanoclusters is known to be the most critical factor for their unique catalytic activity. However, Au nanoclusters sinter rapidly at elevated temperature, losing their catalytic activity. In this study, we have investigated how the rate of sintering can be controlled by adding Pt to Au nanoclusters since pure Pt nanoclusters are less sintered than pure Au due to stronger metal-metal bonds. As a model system, Pt and Au nanoclusters were deposited on a single crystal TiO2(110) substrate and investigated by STM, XPS, LEIS, and TPD in UHV. When Au is deposited on Pt clusters, Pt nanoclusters act as seeds for Au nucleation. However, for Pt deposition on Au, the Au clusters do not nucleate the growth of bimetallic Au-Pt clusters. The extent of cluster sintering at 1000K decreases with increasing Pt composition within the clusters. Intermixing of Au and Pt occurs readily at room temperature; for bimetallic Au-Pt clusters prepared by depositing Au on Pt, the surface contains a significant fraction of Pt atoms, despite immiscibility of Au and Pt and lower surface free energy of Au.

9:20am **SS1-MoM5 The Fabrication and Reactivity of Anchored Metal Nanoparticles on TiO_2(110)**, ***M. Bowker***, Cardiff University, UK**INVITED**

We have investigated the interaction of Pd particles with the TiO2(110) surface in some detail using high temperature STM, XPS and a molecular beam reactor. Upon formation of nanoparticles at low anneal temperatures (<600K), a high adsorption probability of CO is found, much higher than expected from the fraction of the surface covered by Pd. This is due to the influence of a precursor state; this is a weakly-held form of CO on the support, which has a short lifetime at 300K (~ 1 micros), but which can nevertheless find nearby Pd nanoparticles (at which it gets trapped) by surface diffusion, which is extremely efficient. Nonetheless the CO is actually held more weakly on the nanoparticles than on bulk Pd, due, we believe, to modifications of the Pd by the presence of Ti in the surface of the particle. Upon heating to only 700K, the CO is further destabilised on the Pd, such that the sticking probability and uptake become very low; this is NOT due to sintering which is minimal at this temperature. Investigation by XPS shows that Ti has migrated onto the surface of the Pd as the surface was heated. From the chemical shifts this Ti is probably present as surface TiO, with Ti in the 2+ oxidation state. STM shows that, at least for surfaces annealed above 700K, beautiful ordered structures of the surface layer are formed, with large unit cells. The two main structures are a pinwheel and a zig-zag. In this talk I will try to assign the detailed structures of these layers which is proposed to be intermetallic-like, with the two structures being very specific intermetallics with Pd:Ti ratios of 1:1 and 2:1 respectively. This material causes the loss of activity seen for CO adsorption and for catalysis.

10:20am **SS1-MoM8 Enhanced Bonding of Gold Nanoparticles on Oxidized TiO_2(110)**, *S. Wendt*, ***J. Matthiesen***, *D. Matthey, J.G. Wang, R. Schaub, E. Lægsgaard, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark

Finding of distinctive catalytic properties of dispersed gold nanoparticles on oxide supports has stimulated extensive research activities, and a general consensus now exists on several aspects of this system. The size of the gold particles significantly affects the catalytic activity, and the gold clusters must be smaller than 5 nm for high catalytic activity.[1,2] The choice of the oxide support influences the catalytic activity, so there is a strong 'support effect' in addition to the 'size effect'.[1] However, the relation of the adhesion properties of nanosized gold with catalytic activity is still unresolved. We studied the nucleation of gold clusters on TiO_2(110) surfaces in three different oxidation states by high-resolution scanning tunneling microscopy (STM). The three TiO_2(110) supports chosen were (i) reduced having bridging oxygen vacancies, (ii) hydrated having bridging hydroxyl groups, and (iii) oxidized having oxygen ad-atoms.[3] At room temperature gold clusters nucleate homogeneously on the terraces of the reduced and oxidized supports, while on the hydrated TiO_2(110) surface clusters form preferentially at the step edges. From interplay with density functional theory (DFT) calculations, we identified two different gold - TiO_2(110) adhesion mechanisms for the reduced and oxidized supports. The adhesion of gold clusters is strongest on the oxidized support, and the implications of this finding for catalytic applications are discussed.[4]

[1] Meyer, R., Lemire, C., Shaikhutdinov, Sh.K., Freund, H.-J., Gold Bulletin 37 (2004) 72-124.

[2] Valden, M., Lai, X., Luo, K., Guo, Q., Goodman, D.W., Science 281 (1998) 1647-1650.

[3] Wendt, S., Schaub, R., Matthiesen, J., Vestergaard, E.K., Wahlström, E., Rasmussen, M.D., Thostrup, P., Molina, L.M., Lægsgaard, E., Stensgaard, I., Hammer, B., Besenbacher, F., Surf. Sci. 598 (2005) 226-245.

[4] Matthey, D., Wang, J. G., Wendt, S., Matthiesen, J., Schaub, R., Lægsgaard, E., Hammer, B., Besenbacher, F., Science 315 (2007) 1692 - 1696.

10:40am **SS1-MoM9 Tuning the Properties of Gold Atoms and Clusters on MgO by Film Thickness**, ***T. Risse***, *M. Sterrer, M. Heyde, N. Nilius*, Fritz-Haber-Institut der MPG, Germany, *G. Pacchioni*, Universita di Milano-Bicocca, Italy, *H.-J. Freund*, Fritz-Haber-Institut der MPG, Germany

The catalytic activity of Au clusters deposited on oxide supports is extensively studied in recent years. There is evidence that the charging of Au particles may play an important role in this respect. In particular, combined theoretical and experimental evidence shows that nucleation of Au clusters at point defects of MgO leads to a charging of the particles and this may be connected with the enhanced catalytic activity in low-temperature CO oxidation. According to theoretical calculations a similar charging is expected for Au deposits on very thin MgO films of a few monolayer.[1,2] In this contribution we present a low-temperature scanning tunneling microscopy investigation on the properties of gold atoms and clusters adsorbed on ultrathin MgO films grown on a Ag(001) single crystal surface. The gold adsorption was studied at 5-10 K using MgO films of different thickness to provide experimental evidence for the theoretically predicted charging of gold atoms and clusters on very thin films. The adsorption of Au on a 3 ML thin MgO film leads to a preferential ordering of Au atoms revealing a repulsive interaction between the Au atoms which is consistent with the expectation for charged atoms. On the contrary Pd atoms which are predicted to be neutral show a statistical nucleation behavior. In addition, it is found that the adsorption sites of Au atoms change when changing the thickness of the MgO film from 8 ML to 3 ML perfectly in line with the theoretical predictions. Whereas Au clusters on bulk MgO or thick films are expected to grow as 3-dimensional islands, their counterparts on thin MgO films are expected to from 2-dimensional islands. Annealing experiments of Au deposited at 5-10 K show that this crossover in dimensionality does exist for Au particles in the thickness range of 3 ML to 8 ML of the MgO films.

[1] G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005).

[2] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

11:00am **SS1-MoM10 Catalytic Dehydration of Alcohols on TiO$_2$(110) and (WO$_3$)$_3$/TiO$_2$(110) Model Catalysts[1]**, ***Y.K. Kim***, University of Texas at Austin, *B.D. Kay*, Pacific Northwest National Laboratory, *J.M. White*, University of Texas at Austin, *Z. Dohnálek*, Pacific Northwest National Laboratory

The catalytic dehydration of alcohols on rutile TiO$_2$(110) and on monodispersed (WO$_3$)$_3$ clusters on TiO$_2$(110) was studied using reactive scattering and temperature-programmed desorption (TPD). Two distinct dehydration channels, one at low temperature (LT) and the other at high temperature (HT), are observed on TiO$_2$(110). The LT and HT channels are shown to be related to reactions on the Ti^{4+} rows and on the vacancies of bridge-bonded oxygen (BBO) rows, respectively. The dehydration rates are shown to be influenced by the inductive and steric effects introduced by the hydrocarbon chains of the reacting alcohols. For the (WO$_3$)$_3$/TiO$_2$(110) model catalyst, we find a dramatic increase in catalytic activity compared to bare TiO$_2$(110). The quantitative correlation between the coverage of (WO$_3$)$_3$ clusters and the dehydration yield indicates that the W^{6+} Lewis acid sites are involved in the reaction.

[1] The research described in this presentation 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.

11:20am **SS1-MoM11 Hot Electron Flow and Chemical Reactivity on Colloid Nanoparticles on Metal-Semiconductor Catalytic Nanodiodes**, ***J.Y. Park***, *J.R. Renzas, B. Hsu, Y. Zhang, H. Lee., P. Yang, G.A. Somorjai*, Lawrence Berkeley National Laboratory and University of California, Berkeley

Atomic or molecular processes in metals can generate flows of hot electrons with kinetic energy of 1-3 eV, and mean free path of about 10 nm. The electron flow is detected as a chemicurrent if the excess electron kinetic energy generated by the exothermic reaction is larger than the effective Schottky barrier formed at the metal-semiconductor interface. Detection of hot electron flows could allow us to understand the role of electronic energy dissipation and charge transport through the metal-semiconductor interface in exothermic metal catalyzed reactions. We fabricated nanoparticle-nanodiode hybrid systems composed of metal (Pt and Rh) nanoparticles (size 3-13 nm), an Au thin film (2 nm thick), and TiO$_2$. The interface between Au and TiO$_2$ forms a Schottky barrier with an energy barrier of 1.0 eV. Hot electrons are generated on the surface of the metal nanoparticles, scatter into the Au thin film, and go over the energy barrier between Au and TiO$_2$. The overall thickness of the metal assembly (nanoparticles and Au thin film) is comparable to the electron mean free path, resulting in the ballistic transport of hot electrons through the metal and into the semiconductor. The chemicurrent and chemical reactivity we measured using nanoparticles with sizes of 3-14 nm, and with various capping agents (citrate (trisodium citrate), PVP (polyvinylpyrrolidone), Ctab (tetradecyltrimethylammonium bromide), hexadecylamine, and hexadecylthiol) during catalytic CO oxidation (at pressures of 100 Torr of O$_2$ and 40 Torr of CO at 373 ~513 K). We found that chemicurrent and chemical reactivity depend significantly on the choice of capping layer. While nanoparticles with the citrate capping agent exhibit the highest chemical reactivity and chemicurrent, hexadecylamine, and hexadecylthiol capped nanoparticles shows low reactivity and chemicurrent. We will discuss the size dependence of nanoparticles on the chemicurrent yield. The influence of charging of capping layers on the hot electron transport during the catalytic reaction will be also discussed.

11:40am **SS1-MoM12 TiO$_2$ with Buried Ag Nanoclusters for Photocatalysis[1]**, *F. Wang, A.K. Sekharan, B.M. Watson, O. Kizilkaya, P.T. Sprunger*, ***R.L. Kurtz***, Louisiana State University

Many metals readily form nanoclusters on TiO$_2$ and these clusters can have unusual optical and catalytic properties. The lifetime of these clusters can be limited when exposed to an electrochemical environment, so it can be desirable to bury these metallic clusters in a protective oxide layer. Although the clusters do not participate directly in chemical reactions, optical excitations allow them to provide hot electron-hole pairs to the near surface region to stimulate surface chemistry. We will present a multiple-technique surface study of overcoating Ag nanoclusters on TiO$_2$(110) with titania using STM, EELS and synchrotron-based resonant photoemission. STM measurements show that Ag readily forms 5-10 nm clusters on TiO$_2$(110) and EELS measurements show that the bare clusters on TiO$_2$(110) exhibit a sharp plasmon resonance at 3.7 eV. As the cluster density increases, the underlying substrate bandgap is reduced while the bandgap excitation cross-section increases. These Ag clusters are then buried by coating with a thin layer of Ti that is subsequently oxidized. Within the dielectric medium of the oxide, the plasmon resonance is broadened and red-shifted as shown by EELS. Synchrotron-based resonant photoemission has been used to study the electronic structure of the clusters, both bare and with and the titania overcoat. The valence electronic structure and the origin, whether Ti or Ag-induced, of the bandgap defect states within the titania are identified by tuning over photoemission resonances. The role of these bandgap states in determining the surface optical properties and photochemistry will be discussed.

[1] We would like to acknowledge the support of the LSU CAMD synchrotron light source and the support of NSF through CHE-0615606.

Surface Science

Room: 611 - Session SS2-MoM

Surface Structure, Growth, and Etching of Silicon and Germanium

Moderator: S. Chiang, University of California, Davis

8:00am **SS2-MoM1 Combined Scanning Tunnelling Microscopy and Stress Measurements to Elucidate the Origins of Surface Forces During the Oxidation of Si(111)-7x7**, ***N.T. Kinahan***, *D.E. Meehan*, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, *T. Narushima, K. Miki*, National Institutes of Natural Sciences, Japan, *J.J. Boland*, CRANN & Trinity College Dublin, Ireland

The oxidation of silicon surfaces has been widely studied due to its scientific and technological importance. However, despite extensive experimental and theoretical studies, the details of the oxidation reaction are not yet fully understood. It has recently been suggested that surface stress measurements may prove useful in elucidating this and related issues. In the case of adsorption on solid-state surfaces, stress arises primarily from differences in atomic size and electronegativity, in addition to unit cell expansion due to the incorporation of atoms into the substrate. Here, we study the surface stress evolution encountered during oxidation of the Si(111)-7x7 surface using a novel system combining both surface stress measurement and scanning tunnelling microscopy (STM) capabilities.[1,2] The former measurement is based on the displacement of a large silicon cantilever sample, while the latter measurement permits direct observation of the atomic structure of the same cantilever sample. We show that the initial oxidation of the Si(111)-7×7 surface at room temperature involves two compressive stress stages with different growth signatures. The atomic scale origins of the measured surface stress evolution will be discussed and supported via complementary STM data. In particular, we demonstrate that the initial rapid rise in compressive stress is associated with selective oxidation of the faulted-half units of the 7x7 reconstruction.

[1] T. Narushima, N.T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 76 095113 (2005).

[2] T. Narushima, N.T. Kinahan, J. J. Boland, Rev. Sci. Instrum. 78 053903 (2007).

8:20am **SS2-MoM2 Kinetic Monte Carlo Simulation of Oxide Island Formation and Step Pinning during Etching by Oxygen of Vicinal Si(100)**, ***M. Albao***, National Sun Yat-Sen University, Taiwan, *J.W. Evans*, Iowa State University, *F. Chuang*, National Sun Yat-Sen University, Taiwan

A lattice-gas model was developed incorporating a recently observed oxide island shape transformation from linear to two-dimensional[1] during initial stages of oxidation of Si(001). Kinetic Monte Carlo (KMC) simulations of such a model offers clues as to the nature of the pinning of steps and their subsequent transformation into finger-like structures[2,3] during prolonged etching of vicinal Si(100) by exposure to molecular oxygen. KMC results suggest that the initial linear shape of oxide clusters might allow them to protect slightly wider sections of the steps against erosion than would a similar 2D island of the same number of atoms. This proposal follows from comparison of the width of the "fingers" that subsequently evolved from the pinning by these two cluster types. Thus, the initial shape of the islands as much as their size appears to be key in stabilization and long-term survival of fingers. Additionally, the same model was used to uncover potential mechanisms for boosting oxide cluster nucleation and thus cluster populations at step edges. In turn, this increased concentration of oxide clusters at the steps sets the stage for increased chances of pinning.

[1] H. Togashi, H. Asaoka, T. Yamazaki, M. Suemitsu, Jpn. J. App. Phys. 44 (2005) 1377.

[2] J.V. Seiple and J. Pelz, Phys. Rev. Lett. 73 (1994) 999.

[3] M.A. Albao, D.-J. Liu, M.S. Gordon, and J.W. Evans, Phys. Rev. B 72 (2005) 195420.

8:40am **SS2-MoM3 Etching of Si(100) Surfaces in H_2O**, ***I.T. Clark***, *B.S. Aldinger, A. Gupta, M.A. Hines*, Cornell University

An etchant that produces atomically flat or near-atomically flat Si(100) surfaces has long been sought by the microelectronics industry. While a number of aqueous bases are known to produce atomically flat Si(111) surfaces, a comparable etchant for the commercially important Si(100) surface has not been demonstrated. We will present the results of a combined chemical and morphological investigation into the etching of Si(100) surfaces by room- temperature deoxygenated water. Over the course of several hours of etching, the surface develops a surprisingly homogeneous 4-fold symmetric cross-hatch motif dominated by orthogonal "stripes" running along {110} directions. Simultaneous spectroscopic investigations demonstrate the development of a microfaceted H-terminated surface, consisting of Si{111}, Si{110} and Si{100} planes. A simple model for the development of highly homogeneous surfaces during H_2O etching will be discussed

9:00am **SS2-MoM4 Super-Saturation Etching on Si(100)-(2x1) via Cl Insertion: A New Reaction Pathway**, ***A. Agrawal***, *R.E. Butera, J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy to show that Cl_2 dosing of Cl-saturated Si(100)-(2x1) at elevated temperature leads to uptake beyond "saturation". The surface then evolves along a new etching pathway that involves insertion of extra Cl, denoted Cl(i), in Si-Si dimer bonds or back-bonds, diffusion of Cl(i) to form the volatile precursor, and pairwise desorption of $SiCl_2$. Insertion is made possible by chemisorption that is mediated by dangling bond sites. Upon dissociation, one Cl atom adsorbs at the dangling bond while the other inserts with ~10% probability. The dangling bonds required for insertion are produced by phonon-activated electron-stimulated desorption of atomic Cl from the surface. These studies establish a novel form of Cl_2 dissociative chemisorption, and this should stimulate further investigations into surface dynamics.

9:20am **SS2-MoM5 The Growth and Evolution of Ag on Ge(111) Studied by LEEM**, ***J.A. Giacomo***, *S. Chiang*, University of California, Davis

The clean Ge(111) surface has a c(2x8) reconstruction at room temperature. When Ag is dosed onto the surface two main structures are found, a low coverage (4x4) and a higher coverage $(\sqrt{3}x\sqrt{3})$R30° phase. We have used the real-space imaging capabilities of a low energy electron microscope (LEEM) to investigate the growth, phase transitions, and dynamics of these phases. The (4x4) phase begins to form at temperatures above 200°C and coverages above 0.1ML. LEEM videos show the (4x4) phase grows with a high dependency on surface steps. This dependency on steps has been attributed to the high diffusivity of Ag adatoms along the step edges[1]. The growth of the (4x4) phase also produces faceting of the surface which is shown in the LEEM images as the (4x4) phase grows from the steps. At higher coverages the (4x4) phase transitions into a $(\sqrt{3}x\sqrt{3})$R30° phase. LEEM data of the growth of this phase shows little dependence on the steps with the phase propagating over the terraces. This growth pattern is attributed to the higher diffusivity of Ag adatoms across the (4x4) layer[1] reducing the advantage of diffusion along the steps. Near the desorption temperature, we have found an interesting phase transition as domains of $(\sqrt{3}x\sqrt{3})$R30° abruptly transform to the lower coverage (4x4) and then to a disordered phase. The disordered phase produces no contrast in the LEEM images but if the condensed phases are allowed to completely disappear and the sample is then immediately cooled the (4x4) and $(\sqrt{3}x\sqrt{3})$R30° phases recondense on the surface. This indicates that the Ag has not completely desorbed and is still present on the surface in a disordered phase.

[1] E. Suliga and M. Henzler, Journal of Physics C-Solid State Physics 16, 1543 (1983).

9:40am **SS2-MoM6 Chemical Vapor Deposition of Boron Carbo-nitride as a Passivation Film for Ge Surfaces**, ***P.R. Fitzpatrick***, *J.G. Ekerdt*, The University of Texas at Austin

As electronic device dimensions are scaled down Ge is receiving considerable attention as an alternative to Si. The primary motivation is the higher charge carrier mobility in Ge compared to Si. However, the Ge/GeO_x interface is chemically and electrically unstable. This work investigates the ability of boron carbo-nitride (BCN) films to passivate single crystal Ge surfaces and Ge nanowires. The BCN films are deposited by thermal chemical vapor deposition (CVD) using dimethylamine borane with NH_3 and C_2H_4 coreactants. Adjustments to the gas composition during CVD make it possible to tune the BCN stoichiometric composition, constituent bonding, and dielectric constant. Ion scattering spectroscopy (ISS) and x-ray photoelectron spectroscopy (XPS) were used to determine the minimum thickness of BCN resulting in a continuous film on Si(100) and Ge(100) substrates. Si(100) was chosen to develop the experimental protocol because of its well-documented surface chemistry. To determine film continuity using ISS, the ratio of the post-BCN substrate signal (either Si or Ge) to the predeposition bare substrate signal was plotted as a function of BCN thickness (determined by XPS peak attenuation for Si and spectroscopic ellipsometry for Ge). Due to the high surface sensitivity of ISS, a continuous BCN film should result in complete attenuation of the substrate signal. BCN becomes continuous at ~2.5nm when grown on Si(100) and ~3.5nm when grown on Ge(100). Differences in the BCN/Si and BCN/Ge interface were examined by depth profiling to understand how interface reactions affect film nucleation. A series of ISS scans gradually sputters the BCN, and XPS scans following each ISS scan track the atomic composition of BCN until the Si or Ge substrate is reached. In both cases the film composition at the substrate interface drastically differs from the bulk composition ($BC_{0.7}N_{0.1}$), with N dominating the B and C contributions at the interface. Nitrogen accumulation is much more pronounced on Si. The BCN film at the BCN/Si interface is comprised of ~70% N whereas the film at the BCN/Ge interface is only ~40% N. XPS was used to determine BCN-coated Ge's ability to withstand oxidation by monitoring changes in the Ge 2p and Ge 3d oxidation states with increasing ambient exposure time. A discontinuous 2.0nm BCN film slows, but does not prevent, Ge oxidation. A continuous 3.5nm BCN film shows no oxidation of Ge following 2 weeks ambient exposure.

10:20am **SS2-MoM8 Novel Superstructure of Thin Pb Film on Si(111) Induced by the Interplay of Quantum Well States and Interfacial Adsorbates**, ***A.A. Khajetoorians***, *H. Eisele, S.Y. Qin, C.-K. Shih*, The University of Texas at Austin

Epitaxial thin Pb films on Si(111) are well known to exhibit pronounced QSE manifested by the phase matching of the Fermi wavelength and the layer thickness, giving rise to bilayer oscillation as well as a re-entrant quantum beats of longer periodicity. Such quantum oscillation phenomena have been observed in preferred film thickness, the location of quantum well states, as well as superconductivity. This work reveals yet another intriguing phenomenon manifested by the QSE: Formation of a novel superstructure resulting from the interplay of the quantum well state of the metal film and the cesium adsorbates at the interface of Si(111) substrate and Pb thin film overlayers. The superstructure consists of a periodicity of about 8 nm, incommensurate with the Si(111) 7x7 periodicity. Moreover, there is a dependence of the actual periodicity and orientation on the film thickness. This work is supported is supported by: IGERT-NSF: DGE-054917; FRG: (DMR-0306239, DMR-0606485), Alexander von Humboldt Foundation.

10:40am **SS2-MoM9 Controlled Selforganization of Atom Vacancies in Monatomic Gallium Layers**, ***P.C. Snijders,*** Delft University of Technology, The Netherlands (now at ORNL), *E.J. Moon,* University of Tennessee, Knoxville, *C. Gonzalez, J. Ortega, F. Flores,* Universidad Autonoma, Madrid, Spain, *H.H. Weitering*, University of Tennessee, Knoxville, and Oak Ridge National Laboratory

Ga adsorption on the Si(112) surface results in the formation of pseudomorphic Ga atom chains. Compressive strain in these atom chains is relieved via creation of adatom vacancies.[1] These vacancies selforganize into meandering vacancy lines (VLs) similar to the well-known nx2 superstructures for Ge on Si(100).[2] We show that the average spacing between these line defects can be experimentally controlled continuously, within limits, by adjusting the chemical potential μ of the Ga adatoms. The small VL spacings in this system result in significant VL correlations that cannot be captured within a mean field analysis of the VLs.[2] We derive a conceptually new lattice model that quantitatively connects Density Functional Theory (DFT) calculations for perfectly ordered structures, with the fluctuating disorder seen in experiment and the experimental control parameter μ for this correlated VL system. Applying this model to statistical data from large scale STM images, we calculate the (repulsive) VL interaction energy and the kink energy. This hybrid approach of lattice modeling and DFT can be applied to other examples of line defects in hetero-epitaxy, especially in cases where correlation effects are significant and a mean field approach is not valid.[3]

[1] C. Gonzalez, P.C. Snijders, J. Ortega, R. Perez, F. Flores, S. Rogge, and H.H. Weitering, Phys. Rev. Lett. 96, 126106 (2004), P.C. Snijders, S. Rogge, C. Gonzalez, R. Perez, J. Ortega, F. Flores, and H.H. Weitering, Phys. Rev. B 72, 125343 (2005).

[2] X. Chen, F. Wu, Z. Zhang, and M.G. Lagally, Phys. Rev. Lett. 73, 850 (1994).

[3] Part of this work (HHW) was supported by the US DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, through Oak Ridge National Laboratory which is managed by UT-Battelle, LLC.

11:00am **SS2-MoM10 Gold Nanowire Formation on Si(110) Studied by SPM**, ***M. Yoshimura,*** *M. Tanaka, K. Ueda*, Toyota Technological Institute, Japan

Recently, nanostructures such as quantum dots and wires have been focused because of their exotic properties originated from the confinement of electrons, such as Coulomb blockade, charge density waves, spin density waves, etc. Several chain structures have been observed for Au/Si systems such as Au/Si(557).[1] For the Au/Si(110) system, Yamamoto reported a variety of surface phases using reflection high-energy electron diffraction (RHEED),[2] and only one phase, 2×5 structure, has been investigated in real space by scanning tunneling microscopy (STM).[3] In this study, we aim to clarify the relationship between several surface phases of Au/Si(110) by high-resolution STM and atomic force microscopy (AFM). On the basis of high-resolution SPM images, we propose structural models for the phases and discuss the mechanism of nanowire formation. At 0.2-0.3 ML coverage, up-and-down structure of the clean Si(110) surface is destroyed, and 1×2 structure was clearly confirmed by FFT analysis, corresponding to nucleation of the nanowire. It is suggested that (110) facets develop in the Si(110) surface. The density of the nanowires increases with Au coverage to 0.25 ML. The spacing between the wires varies from 5a to 10a (a:unit length along the [-110] direction of Si(110)). At the coverage of 0.30 ML, it becomes constant at 5a, showing 2×5 surface phase. The nanowire consists of double rows with fluctuation character. The detailed atomistic processes of nanowire formation, as well as possible atomic structure models, are discussed.

[1] H. W. Yeom et al., Phys. Rev. B 72, 035323 (2005).

[2] Y. Yamamoto, Surf. Sci. 271, 407 (1992).

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11:20am **SS2-MoM11 Faceting and Band-Flattening Induced by Sb-Indiffusion into Si(5 5 12)-2x1**, ***H. Li,*** *H. Kim, J.M. Seo*, Chonbuk National University, Korea

Initial stages of antimony (Sb) adsorption on the Si(5 5 12)-2x1 surface have been studied by STM/STS in order to understand interfacial reaction between adsorbed Sb atoms and the Si template with one-dimensional (1-D) symmetry. It has been found that there are two distinct steps, Sb indiffusion and preferential adsorption, at the initial Sb adsorption on Si(5 5 12)-2x1 held at 600 C. Initially, deposited Sb atoms (up to 0.15 ML) diffuse into the subsurface and cause indirect Si deposition. As a result a π-bonded Si chain is firstly formed on dimer/adatom row like homoepitaxy, and the surface reconstruction gradually changes from a (5 5 12) terrace to (337) terraces with (113) steps. The band is flattened by 0.2 eV by subsurface doping with indiffused Sb atoms. As soon as the subsurface Sb sites are saturated by indiffused Sb atoms, additionally deposited Sb atoms are preferentially adsorbed along the upper (113)-step edges and form 1-D Sb wires with a spacing of about 10 nm which corresponds to two periodic lengths of the original (5 5 12) surface. Once Sb-adsorption sites, (113) steps, are saturated, deposited Sb atoms cluster for themselves and do not contribute to nanowire fabrication. From the present studies, it has been found that both Sb indiffusion and preferential adsorption stabilize the high-index surface through relieving surface strain by way of either inserting or attaching Sb atoms, but once such surface strain is relieved, the 1-D growth mode also terminates.

11:40am **SS2-MoM12 Surface Reconstructions Induced by Calcium Fluoride Growth on Si(001)**, ***Y. Cui,*** *J. Nogami*, University of Toronto, Canada

The growth of Calcium Fluoride (CaF_2) on Silicon has been widely studied since it grows epitaxially on Si with small lattice mismatch (0.6% at room temperature). There is an extensive literature on CaF_2 growth on Si(111) where a natural epitaxial relationship results in flat thin films with low defect density. However, very little work has been reported for CaF_2 on Si(001). It is known that CaF_2 grown on Si(001) forms either compact islands or long ridges in the Stranski-Krastanow mode.[1,2] STM images of the wetting layer show an inhomogeneous row like structure.[3] In this STM study, 2x3 or 2x4 periodicities were identified in the first layer depending on CaF_2 coverage and growth temperature. The LEED pattern shows an unusual combination of spots and streaks with variable line width and intensity. The configuration of the pattern is caused by the alignment of surface unit cells and phase disorder. The nucleation of CaF_2 small areas is also seen and paves a way to further studies on 3D insulator nanowires. Finally the parallels between these results and the ones obtained for growth of CaF_2 on Si(111) is discussed.

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[2] Pasquali, L.; D'Addato, S.; Selevaggi, G.; Nannarone, S.; Sokolov, N.S.; Suturin, S.M.; Zogg, H.: Nanotechnology, v 12, n 4, Dec. 2001, p 403-8

[3] Sumiya, T.; Miura, T.; Fujinuma, H.; Tanaka, S.: Surface Science, v 376, n 1-3, 10 April 1997, p 192-204.

Surface Science

Room: 608 - Session SS1-MoA

Water-Surface Interactions

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

2:00pm **SS1-MoA1 Water Adsorption on Ruthenium (0001) Pre-covered with Atomic Oxygen Studied by Scanning Tunneling Microscopy**, ***T.K. Shimizu***, *A. Mugarza,* Lawrence Berkeley National Laboratory, *P. Cabrera-Sanfelix,* Donostia International Physics Center, Spain, *D.S. Portal,* Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Spain, *A. Arnau,* Departamento de Física de Materiales UPV/EHU, Spain, *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

The adsorption of water on a Ru(0001) surface pre-covered with atomic oxygen forming a (2x2) structure was studied using low temperature scanning tunneling microscopy (STM). Below 0.25 ML, water adsorbs molecularly on top Ru sites within the (2x2) superstructure and forms two hydrogen bonds with pre-adsorbed O atoms. Because of the additional H-bonding, the water molecules are more strongly bound than those on the bare Ru metal. Water dissociation is completely blocked on the (2x2)-O/Ru surface and annealing results only in molecular desorption in the temperature range of 140-230 K. This is in contrast to the water adsorption on Ru with smaller pre-coverage of oxygen. These results will be discussed in light of current models relating water binding to the hydrophillicity and hydrophobicity of the underlying metal surfaces.

2:20pm **SS1-MoA2 Vibrational Study of Individual Water Dimers on Pt(111) using Scanning Tunneling Microscope**, ***K. Motobayashi,*** RIKEN, The University of Tokyo, Japan, *C. Matsumoto,* Gakushuin University, Japan, *Y. Kim,* RIKEN, Japan, *M. Kawai*, RIKEN, The University of Tokyo, Japan

The adsorption and diffusion of water molecules on metal surfaces play an important role in various fields of surface science, such as electrochemistry, heterogeneous catalysis, corrosion, and so on. Although the adsorption structure of water on a variety of metal surfaces at low coverage has been extensively investigated with various techniques, still unclear is the microscopic feature of adsorbed isolated water molecules. On the other hand, Vibrational spectroscopy methods have been used as powerful tools to get information of bond specific interactions, but in spite of that, the spatial resolution and sensitivity of conventional methods are not sufficient to detect vibrational signals from individual water monomers and dimers. To solve these problems, we investigated and report microscopic and vibrational study of adsorption behaviors of individual water molecules, especially water dimers, on Pt (111) by use of the scanning tunneling microscopy (STM) at 4.7 K. The Pt (111) single crystal surface was dosed with a small amount of water molecules (< 0.01 ML) at a temperature lower than 20 K. This temperature is low enough to prevent water molecules from thermal processes, such as diffusion, desorption and chemical reaction, on the surface, so that one can easily observe isolated water monomers and without forming large clusters. A water dimer appears as a flower like protrusion in the STM images, while a water monomer as a single protrusion as shown in Figure 1. It can be explained as one of the water molecules in a dimer rotating around the other. Indeed, we have succeeded in forming a dimer by manipulating two monomers with an STM tip, and also breaking a dimer into two monomers by inducing pulse bias. We obtained vibrational information by analyzing diffusion behavior of individual water dimers using STM, which method is so called "Action spectroscopy". The result of this measurement provides us not only the information of bond specific interaction but also the detailed features of adsorption structure. We found a kind of hydrogen bonding between one water molecule and Pt surface atoms in adsorption structure of a dimer.

2:40pm **SS1-MoA3 Dissociation of Water on Modified Transition Metal Surfaces**, ***G. Held***, University of Reading, UK **INVITED**

Water dissociation on surfaces of late transition metals has been a topic of intense discussion in the last few years.[1-4] It is remarkable in this context that different members of the Pt group, which normally show very similar chemical behavior, cause water to react in very different ways. This could be caused by small differences in the surface lattices, affecting the (mis)match with ice-like water layers, or by electronic differences, affecting the balance between inter-molecular hydrogen bonds and water-substrate bonds. Atomic or molecular coadsorbates are convenient means of modifying both types of bonds and were used in a systematic study to address this question. We compare the reactivity of water on clean and O-modified Pd{111}, Ir{111}, Pt{111} and Ru{0001} using LEED, TPD, high resolution XPS and NEXAFS. All four surfaces have the same surface symmetry and very similar lattice constants. Except for Ru{0001}, no dissociation is observed on the clean surfaces, even after prolonged irradiation with X-rays. Small amounts of oxygen, however, cause water to dissociate, whereas high coverages (> 0.25ML) tend to leave water intact with more stable surface bonds than for the clean surfaces.[5] The exception here is Pt{111}, where water dissociates for all oxygen coverages up to saturation. Molecular co-adsorbates, such as CO and methanol tend to inhibit water dissociation. Possible geometrical effects were investigated using Pt{111}, {110} and {531}, these surfaces represent a series with increasing atomic roughness and coordination numbers decreasing from 9 to 6. We could not find any increased reactivity of low-coordinated Pt atoms with respect to the dissociation of water only an increase in the water-substrate bond strength. Small amounts of oxygen promote water dissociation on all three surfaces; a high coverage (exceeding half the saturation coverage) prevents dissociation on Pt{531} and Pt{110}, but not on Pt{111}. These results indicate that dissociation of water on Pt group surfaces depends more sensitively on electronic modifications, as induced by oxygen coadsorption, than on the surface geometry.

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[3] J. Weissenrieder, et al. PRL 93 (2004) 196102;

[4] K. Andersson, et al. PRL 93 (2004) 196101.

[5] M.J. Gladys, et al. CPL 414 (2005) 311.

3:40pm **SS1-MoA6 Crystallization of Thin Amorphous Solid Water Films on Ru(0001) and on CO-precovered Ru(0001)**, ***T. Kondo,*** RIKEN and University of Tsukuba, Japan, *H.S. Kato,* RIKEN, Japan, *M. Bonn,* AMOLF, FOM, The Netherlands, *M. Kawai*, RIKEN and University of Tokyo, Japan

The deposition and the isothermal crystallization kinetics of thin amorphous solid water (ASW) films on both Ru(0001) and CO-precovered Ru(0001) have been investigated in real time by simultaneously employing helium atom scattering, infrared reflection absorption spectroscopy and isothermal temperature-programmed desorption. The modification of the Ru(0001) surface by the pre-adsorption of CO has been found to affect the deposition feature of water layers at the water coverage below ~5 ML: whereas an ordered first layer structure of water is formed on both the bare surface and the surface pre-adsorbed with 0.33 ML CO, a disordered structure is formed when 0.65 ML CO is pre-adsorbed. During ASW deposition, the interaction between water and the substrate depends critically on the amount of pre-adsorbed CO. However, the mechanism and kinetics of the crystallization of ~50 layers thick ASW film were found to be independent of the amount of pre-adsorbed CO. We demonstrate that crystallization occurs through random nucleation events in the bulk of the material, followed by homogeneous growth, for solid water on both substrates with an apparent activation energy of 650 ± 25 meV. The morphological change accompanying the formation of 3D grains of crystalline ice results in the exposure of the water monolayer just above the substrate to the vacuum. Remarkably enough, the appearance of this first water layer occurs already during the crystallization process, on both substrates.

4:00pm **SS1-MoA7 Growth, Structure, and Dynamics of Nanoscale Water Films on Various Substrates**, ***B.D. Kay***, *G.A. Kimmel, N.G. Petrik, Z. Dohnalek, R.S. Smith*, Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on various substrates (Pt(111), Pd(111), C(0001) and FeO(111)) is investigated using temperature programmed desorption, rare gas physisorption, specular helium scattering, and infrared spectroscopy. At low temperatures water forms an amorphous film that wets all substrates studied. Heating the amorphous film, or growth at higher temperatures, results in the formation of crystalline ice. Concomitant with crystallization, the water films form non-wetting three dimensional crystallites on either the bare substrate or a substrate covered by only a single monolayer of water. The experimental results and their implications concerning hydrophobicity and the wetting-dewetting transition will be presented.

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Science Division. The experiment and calculations were performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle.

4:20pm **SS1-MoA8 The H/D Exchange in Water at Surfaces of Ice and on Cu(100) Studied by Infrared Vibrational Spectroscopy and DFT Calculations**, ***P. Uvdal***, *J. Blomquist*, Lund University, Sweden

Proton transfer in water through the reaction $H_2O + D_2O \rightarrow 2HDO$ is one of many intriguing properties of water. We have studied the exchange in water at ice surfaces and on a Cu(100) surface using infrared vibrational spectroscopy. Intact molecules of H_2O and D_2O are observed up on adsorption at 84 K and no H/D exchange is observed in H_2O/D_2O mixtures . By monitoring the O-H (3695 cm^{-1}) and O-D (2730 cm^{-1}) stretches assigned to none-hydrogen bonded water molecules at the surface of the ice we have followed the H/D exchange in the temperature region 84 - 145 K. A clear isotope effect is observed in 4/1 mixtures of H_2O/D_2O or D_2O/H_2O. The majority isotope governs the exchange efficiency. The exchange is completed at 140 K resulting in at total scrambling of the isotopes. The vibrational data is interpreted with the aide of DFT calculations of small water complexes.

4:40pm **SS1-MoA9 Hydrogen Bonding, H/D Exchange and Molecular Mobility in Thin Water Films on TiO_2(110)**, ***G.A. Kimmel***, *N.G. Petrik*, Pacific Northwest National Laboratory

We use the electron-stimulated desorption (ESD) of water from films of D_2O, $H_2{}^{16}O$ and $H_2{}^{18}O$ to investigate hydrogen bonding, H/D exchange and molecular mixing in water films on TiO_2 (110) for coverages ≤ 2 ML. By depositing water on the Ti^{4+} adsorption sites (H_2O_{Ti}) at 190 K using one water isotope and water on the bridge bonded oxygen sites (H_2O_{BBO}) at T ≤ 70 K using a different isotope, films with no appreciable mixing of the isotopes between the layers can be prepared. When H_2O_{BBO} is deposited at T > 70 K, partial or complete mixing of the layers occurs depending on the temperature and time. H/D exchange between the first and second water layers occurs at ~15 K lower temperatures than $H_2{}^{16}O/H_2{}^{18}O$ exchange. Isothermal experiments demonstrate that the mixing occurs with a distribution of activation energies centered on 0.29 ± 0.07 eV (0.26 ± 0.07 eV) for $H_2{}^{16}O/H_2{}^{18}O$ (H/D) exchange. While these distributions of activation energies are relatively narrow, they have a profound affect on the kinetics. The results demonstrate that H_2O_{BBO} is hydrogen bonded to H_2O_{Ti}. Since the lateral distance (0.325 nm) for atop adsorption at these sites is too large for hydrogen bonding, one (or both) of the adsorbates must be laterally displaced toward the other in agreement with theoretical predictions.

5:00pm **SS1-MoA10 Vicinal and Interfacial Water Structure of Non-Fouling Poly(ethylene glycol) and Sulphobetaine Self Assembled Monolayers**, ***M.J. Stein***, *B.D. Ratner*, University of Washington

Poly(ethylene glycol) (PEG) and sulphobetaine (SB) are currently used in the formation of non-fouling surfaces. As yet, an understanding of the water phase effects in the vicinal realm of these surfaces and their impact on protein resistance remains imperfect. In this work, we present analysis of mixed self-assembled monolayers (SAMs) with either the PEG or SB functionality and the impact of hydration on both monolayer and vicinal water structure using multiple surface analytical techniques. The degree of protein resistance in the SAMs was modified through successive addition of diluent hydrophobic thiols to achieve a broader spectrum of protein resistant surfaces as measured through radio-labeled protein adsorption. The hydrophilic diluents yielded lower amounts of protein adsorption overall for both PEG and SB surfaces. However, the overall trends in protein adsorption differed for the two non-fouling thiols. SB yielded lowest adsorbed fg, alb, and lys when assembled in a 50:50V concentration with 11-mercaptoundecan-1-ol; whereas, pure PEG SAMs yielded the lowest levels of adsorbed protein. The packing density and chemical composition of the SAMs were examined by XPS, as well as ToF-SIMS. The orientation of the SB head groups was confirmed through angular XPS revealing a nearly horizontal head group. This contradicted ellipsometric thickness measurements. PEG data showed no similar contradictions. The terminal hydrophilicity of the groups was characterized through contact angle measurements and followed protein adsorption trends. Unpolarized infrared spectroscopy (FTIR) showed that the stretching frequencies, $\nu CH_{2,asym}$ and $\nu CH_{2,sym}$, of the ultra-nonfouling SB and PEG SAMs decreased and approached 2918 and 2850 cm^{-1}, indicative of a crystalline phase, when hydrated. To study hydration effects, each SAM was exposed to a series of timed D_2O soaks. Band shapes of the composite ν_{OH} band of H_2O obtained were fitted to individual peak components and a ratio of the component band areas from the 3400 and 3200 cm^{-1} regions was utilized to cross-compare samples. A single linear trend between the water peak ratio minima and protein adsorption was obtained for both the PEG and SB SAMs with lower ratios corresponding to higher levels of protein resistance. Using this method, FTIR has been used for the first time to demonstrate a correlation between strongly-bound water structure and protein adsorption.

Surface Science

Room: 611 - Session SS2-MoA

Electronic and Vibrational Structure

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-MoA1 Action Spectroscopy of Single Adsorbate Motions**, ***H. Ueba***, The University of Toyama, Japan **INVITED**

I will discuss an idea of action spectroscopy for a single molecule motion induced by vibrational excitation with a scanning tunneling microscope (STM).[1] A simple formula describing the energy transfer from the vibrational mode excited by tunneling electrons to a reaction coordinate mode through anharmonic coupling to overcome the activation barrier[2,3] is combined with the inelastic tunneling current calculated using the non-equilibrium Keldysh Green's function method. This enables the reaction rate to be calculated as a function of the bias voltage, and is applied to CO hopping on Pd (110)[2] and CCH rotation on Cu(001).[4] I propose that the second-derivative of the reaction rate with respect to the bias voltage gives the density of states of the vibrational mode excited by tunneling electrons,[4] which can not be directly observed with inelastic tunneling spectroscopy because of the negative contribution of the elastic current to the total current, and when a molecule motion is induced by the vibrational excitation.

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[2] T. Komeda et al., Science 255, 2055 (2002).
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2:40pm **SS2-MoA3 Action Spectroscopy of Vibrationally Excited Molecules by Inelastically Tunneled Electrons**, ***Y. Kim***, RIKEN, Japan

The excitation of molecular vibration by means of the inelastically tunneled electrons from the tip of a scanning tunneling microscope (STM) can lead to various dynamical processes at surfaces.[1-5] The vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule but also for investigating how molecular vibration can couple with the relevant dynamical processes. Inelastic electron tunneling spectroscopy with the STM (STM-IETS) has been mainly used for obtaining vibrational spectrum of individual molecules. STM-IETS detects the vibrational modes of a single molecule by measuring the total conductance change resulting from both elastic and inelastic electron tunneling.[2,3] However, the STM-IETS is not applicable to some molecules showing mobile character when they are vibrationally excited by inelastically tunneled electrons during measurement. The response of vibrationally mediated molecular motion to applied bias voltage, namely an "action spectrum", can reveal vibrational modes that are not visible in STM-IETS, because the molecular motion is induced via only inelastic tunneling.[3,5] Thus, the action spectrum would be a candidate for detecting which vibrational mode is actually excited and associated with molecular motions. Here, I discuss the usefulness and selection rules of the two types of single molecule vibrational spectroscopic methods by considering the action spectroscopy as an alternative vibrational spectroscopic method for the STM-IETS through the study of vibrationally mediated molecular motions with a low-temperature STM.

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3:00pm **SS2-MoA4 "Walking" Molecules and their Dynamics and Energetics**, *K.L. Wong, G. Pawin, D.H. Kim,* ***L. Bartels***, University of California, Riverside

Thiol groups, despite being proposed as rigid linker for many molecular electronics applications, anchor aromatic molecules to metal surfaces in a fashion that permits rapid rearrangement of the molecule on the substrate even at temperatures as low as 60K. The aromatic ring of individual benzenethiol molecules experiences a rotation barrier around the substrate linker of ca. 120 meV; even diffusion of the sulfur anchor on the substrate has a barrier of only ca. 150 meV.[1] Placement of two thiol groups in a molecule (9,10-dithionanthracene, DTA) does not increase the diffusion barrier. Rather it renders the moleculeâ?Ts diffusion behaviour on Cu(111) anisotropic, i.e. following a single line on the otherwise threefold symmetric substrate.[2] Density functional theory calculations show, that this behaviour originates from sequential occupation of optimal adsites by each of the two substrate linkers, strikingly resembling bipedal locomotion ("walking"). The resultant linear (uniaxial) motion on the surface can be used for transport of "cargo" molecules across a surface[3] as well as for the exploration of fundamental concepts of chemistry.

[1] K.L. Wong et al., Appl. Phys. Lett. 88, 183106 (2006)

[2] K.-Y. Kwon et al., Phys. Rev. Lett. 95, 166101 (2005)

[3] K.L. Wong et al., Science 315, 1391 (2007)

3:40pm **SS2-MoA6 Feedback-Controlled Single Molecule Surface Chemistry**, ***N.L. Yoder***, *J.S. Fakonas, M.C. Hersam*, Northwestern University

In the past 25 years, the scanning tunneling microscope (STM) has enabled the detailed study of the chemistry and physics of single molecules on surfaces. Electron-driven processes (including desorption and dissociation) are especially advantageous because they offer the possibility of rapidly exciting a molecule far from equilibrium with exceptional spatial localization of the excitation.[1] Attaining precise control over the electron dose requires a method for both detecting the desired events and rapidly terminating the flow of electrons to prevent overdosing. A significant advance in this area was Feedback Controlled Lithography (FCL),[2] which involved the creation of isolated reactive sites on H:Si(100) through the controlled desorption of hydrogen. Since reaction products could also be susceptible to electrons, the ability to both detect a molecular conformational change and immediately terminate the flow of electrons is fundamentally relevant to the study of single-molecule processes. In this study, we apply this technique to the investigation of the byproducts of cyclopentene desorption[3] from clean Si(100). Experiments were performed using a cryogenic ultra-high vacuum (UHV) STM operating at 8 K and 80 K. At low temperatures, cyclopentene molecules are controllably desorbed, and a feedback loop is utilized to detect the desorption event and halt electron flow. At the desorption conditions of –4 V and 2 nA, the desorption reaction alternately results in three distinct surface features: a clean silicon dimer (55 %), a half-dimer dark feature (30 %), and fully darkened silicon dimer (15 %). Additionally, the radial and angular distributions of the byproduct binding sites were also measured. The desorption products were often observed at significant distances from the initial desorption site, with some features as far as 3 dimer rows (~23 Å) away. The dark desorption products are attributed to hydrogen-passivated silicon atoms resulting from the dissociation of a cyclopentene C-H bond and the subsequent bonding of the ejected hydrogen with the reactive silicon surface. Finally, tunneling electrons from the STM tip were used to induce hopping and desorption of hydrogen from the partially passivated silicon dimers.

[1] A. J. Mayne et al., Chemical Reviews 106, 4355 (2006).

[2] M. C. Hersam et al., Nanotechnology 11, 70 (2000).

[3] N. L. Yoder et al., Physical Review Letters 97, 187601 (2006).

4:00pm **SS2-MoA7 Isotope-Specific Deposition of Vibrationally Excited Molecules**, ***D.R. Killelea***, *V.L. Campbell, N.S. Shuman, A.L. Utz*, Tufts University

Direct IR excitation of gas-phase reagents offers a potential means of isotope selective chemical vapor deposition (CVD). A narrow bandwidth IR laser selectively excites a vibrational mode in a single isotopomer of methane. These vibrationally excited molecules are significantly more reactive, enhancing their rate of deposition. Here we present results showing control of the carbon isotopic ratio of surface adsorbates by IR excitation of methane. We recombinatively desorb the methyl fragment deposited on a Ni(111) surface after methane dissociatively adsorbs on the surface. We are able to quantify the yield of both carbon-13 and carbon-12 using a mass spectrometer to measure $^{13}CH_4$ and $^{12}CH_4$ desorbing from the surface. Using a methane molecular beam with the natural abundance of carbon-13 and carbon-12, we are able to achieve an eight-fold enhancement in carbon-13 deposition by exciting less than 0.1% of the methane molecules in the molecular beam.

4:20pm **SS2-MoA8 Ion Effects on the Liquid-Vapor Interface of a Non-Aqueous Solution**, ***M.J. Krisch***, *J.C. Hemminger*, University of California, Irvine, *S. Baldelli*, University of Houston

We find that electrolytes modify the liquid-vapor interface of a non-aqueous solution. A variety of recent studies have observed ion-dependent changes in the surface structure of aqueous electrolyte solutions. In this project, we examine the influence of the solvent by probing the surface structure of non-aqueous electrolyte solutions. Our experiments use surface-specific sum frequency vibrational spectroscopy to obtain information about the liquid-vapor interface. We examine a series of alkali halides in ethylene glycol in which the identity of the anion is varied systematically. The spectra show that the addition of salt modifies solution surfaces to a degree that follows the polarizability of the anion in solution, particularly as seen through changes in the OH bonding stretch. Results are compared to surface tension measurements of the same solutions.

4:40pm **SS2-MoA9 Transport Limitations in Tunneling Spectroscopy of Pentacene on SiC**, ***S. Gaan***, *R. Duca, R. Feenstra*, Carnegie Mellon University

Pentacene (Pn) is a promising material for organic field effect transistors because of its relatively high mobility and its tendency to form ordered structures. In this work we have used scanning tunneling microscopy (STM) and spectroscopy (STS) to probe the electronic properties of Pn thin films. The substrates were hydrogen-etched SiC, oxidized by exposure to 4000 L of molecular oxygen at 700°C. The Pn was deposited from a crucible by vacuum sublimation, with the sample at room temperature. On a large scale, the Pn films display a layered morphology with dendritic edges, consistent with prior results.[1] Within each layer, the molecules form ordered arrangements; it is on these regions that STS was performed. We obtain a HOMO-LUMO gap of about 2 eV.[2] Effects of degradation of Pn molecules were seen in the spectra, producing smearing of the band edges. Using the STM, with various tip-sample separations, widely different currents were injected into the sample in order to probe transport of the charge carriers. The tunnel current was found to saturate at positive bias for all tip sample separations, thus revealing a spreading resistance type of effect in Pn films. In other words, a quasi Fermi level exists in the sample and varies as a function of distance from the apex of the probe tip. In order to determine current saturation at negative bias, we examined the dependence of the current on tip-sample separation, at constant voltage. Significant deviation from ideal vacuum tunneling was observed, which also indicates transport limited tunnel current. To explain the observed transport limitation in the tunnel current we propose a simple two resistor model, one resistor for the vacuum and one for the sample, with the assumption that the sample resistance is constant. With different injection levels and voltages we obtain reasonable fits to the data. Using this model we are able to deduce resistivities of the sample for both filled and empty states, $3.3x10^2$ and $2x10^4$ Ω cm, respectively. Work is underway to interpret these results in terms of possible transport mechanisms in our Pn thin films.

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[2] Repp et. al., Phys. Rev. Lett., 94, 026803 (2005).

5:00pm **SS2-MoA10 Intrinsic Accumulation Layer Quantum Well States and Anomalous Valence Band Dispersion in Indium Nitride**, ***K.E. Smith***, *L. Colakerol, T. Learmonth, P.A. Glans, L.F.J. Piper*, Boston University, *A. Fedorov*, Lawrence Berkeley National Laboratory, *T.D. Veal, C.F. McConville*, University of Warwick, UK, *S. Healy, E.P. O'Reilly*, University College Cork, Ireland, *T.C. Chen, T.D. Moustakas*, Boston University

The valence and conduction band electronic structure in InN thin films has been measured using high resolution Angle Resolved Photoemission Spectroscopy (ARPES). InN exhibits an accumulation layer near the film surface, and our ARPES measurements reveal that the conduction band electrons in the accumulation layer exist in intrinsic quantum well states.[1] We also used ARPES to measure the Fermi surface of these quantum well states, as well as their constant binding energy contours below the Fermi level. The energy of the Fermi level, and the size of the Fermi surface for these quantum well states could be controlled by varying the method of surface preparation. Furthermore, a minimum is observed in the dispersion of the top of the valence band, with the highest measured valence band having an electron-like dispersion at the Brillouin zone center, which is unexpected in the context of earlier measurements and calculations. Valence band holes see a quantum barrier near the surface, and a theoretical analysis using a k.p approach of the influence of this barrier indicates that the anomalous dispersion is most likely due to a negative crystal field splitting in InN, contrary to previous expectations. This work was supported in part by the DOE under RF-06-PRD-001 (subcontract from University of Nevada, Las Vegas), by the NSF under grant number DMR-0311792, and by Science Foundation Ireland. The ALS is supported by the DOE, Materials Sciences Division under contract no. DE-AC03-76SF00098.

[1] 1. L. Colakerol, T.D. Veal, H.-K. Jeong, L. Plukinski, A. DeMasi, S. Wang, Y. Zhang, L.F.J. Piper, P.H. Jefferson, A. Fedorov, T.C. Chen, T. D. Moustakas, C.F. McConville, and K.E. Smith, Phys. Rev. Lett. 97, 237601 (2006).

Surface Science

Room: 608 - Session SS1-TuM

Catalytic Chemistry of Hydrocarbons

Moderator: B.E. Koel, Lehigh University

8:00am **SS1-TuM1 Impact of Surface Analysis in Hydrocarbon Catalysis: Examples from Industry**, ***A.S.Y. Chan***, *S.R. Bare*, UOP - Honeywell

Isomerization of straight chain alkanes to their branched isomers is an important industrial process to upgrade the octane value of gasoline. A solid acid catalyst that is effective for the isomerization of light alkanes is sulfated zirconia. In 1990, Sun Refining and Marketing Co. patented a modified sulfated zirconia catalyst containing transition metals (e.g. Mn, Fe) as promoters. More recently, in 2003, UOP patented an improved catalyst that was promoted by at least one lanthanide. In this talk, we will focus on the surface characterization of model sulfated zirconia catalysts that are Mn-promoted and lanthanide-promoted. By using a combination of X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS), the location of promoters and their subsequent effect on the structure of the zirconia support will be elucidated. In addition, the accessibility of active metal and acid sites on these two promoted catalysts will be discussed. Finally, we will generalize the combined XPS and LEIS studies to provide a more complete picture of other catalytic systems: examples will be drawn from novel zeolites used in alkylation reactions, and Pd-based selective hydrogenation catalysts.

8:20am **SS1-TuM2 The Influence of Steps on the Adsorption, Fragmentation, and Reactions of Ethylene and Ethanol on Rh Surfaces**, ***J.N. Andersen***, *E. Lundgren, A. Resta*, Lund University, Sweden

We have used high resolution core level photoemission to study how the adsorption, fragmentation, and reaction of ethylene and ethanol are influenced by low coordinated atoms found at the steps of vicinal Rh surfaces. The talk is naturally divided in two parts. In part 1, we describe how detailed analysis of the C1s spectra including the vibrational fine-structure of this level often facilitates determination of the adsorbed fragments of these molecules. In part 2, we use this method of identification to monitor the influence of steps. This was done by comparing results from Rh(111) and some of its vicinals. For ethanol adsorption, we find large differences in the fragmentation pattern at 300K between the Rh(111) and the Rh(553) surfaces, in particular, the steps on Rh(553) are found to be very effective in dehydrogenation reactions. We also find differences in the oxidation of ethanol, where Rh(553) is found to be more reactive. For ethylene adsorption we have studied the temperature induced ethylidyne formation and subsequent decomposition. Also in this case do we find that the steps increase the reactivity regarding fundamental reactions involved in both the formation and the decomposition pathways. In addition, comparison between Rh(553) and Rh(322) demonstrated a larger reactivity of (100)-type than of (111)-type micro-facets. Finally, we discuss the importance of the present results in the context of catalytic reactions on small metal particles.

8:40am **SS1-TuM3 Mechanistic Insights on Fischer-Tropsch Synthesis**, ***M. Mavrikakis***, University of Wisconsin - Madison **INVITED**

First-Principles methods can provide useful information regarding detailed reaction mechanisms. In this talk, we will present our recent work on the early steps of Fischer-Tropsch synthesis on iron and cobalt based catalysts. A number of elementary reaction steps leading to CO dissociation and hydrogenation of carbon-containing species have been analyzed both in terms of their thermochemistry and minimum energy paths. A comparison between our results and recent experimental results on realistic FTS catalysts leads to some interesting conclusions, including the role of hydrogen in CO dissociation on Fe and Co catalysts, and the possible role of identified surface reaction intermediates in the FTS polymerization reaction.

9:20am **SS1-TuM5 H Induced CO Dissociation on Nickel Surfaces**, *M.P. Anderson, F. Abild-Petersen, J. Engbaek, O. Lytken, S. Horch, J.H. Nielsen,* Technical University of Denmark*, J. Sehested, J.R. Rostrup-Nielsen,* Haldor Topsoe A/S, Denmark*, J.K. Norskov,* ***I. Chorkendorff***, Technical University of Denmark

The dissociation of CO is both a model test reaction on clean single crystals and a relevant reaction step for industrial methanation. Much attention has therefore been dedicated to understanding the details of the mechanism. First of all, there seems to be a lack of consensus on whether CO can dissociate on Nickel at low temperatures (400 K) in a UHV experiment. In this work we have used a Ni(14,13,13) crystal which is mis-cut in such a way that there is an atomic step for each 26 terrace atoms. We show that CO (which has carefully been cleaned from $Ni(CO)_4$) does not dissociate unless the temperature is larger than 400 K and there are atomic steps present on the surface. If the steps are blocked by sulfur no dissociation could be measured under UHV conditions. The activation energy for dissociation is found to be 1.6 eV, which is slightly larger than that for desorption. This observation is found to corroborate with DFT calculations indicating a barrier for dissociation of 1.7 eV. This is, however, in contrast with the activation energy of 1.07 eV and 1.01 eV observed for the methanation reaction on single crystals and real supported catalysts, respectively. Furthermore, surprisingly small prefactors for those reactions have been reported in both cases. By investigating the possible pathways using DFT, a much lower barrier for CO dissociation of 1.08 eV was identified when considering a COH intermediate. By incorporating this intermediate in the reaction pathway, the low activation energy and low prefactors can be explained in terms of a COH intermediate dissociating on step sites both in the single crystal experiments and on the nanoparticles constituting the real catalysts. In the latter case the conclusion is further confirmed by investigations of the relation between the particle size and the catalytic rate, where a strong deviation from a simple surface area effect is found.

9:40am **SS1-TuM6 Density Functional Theory Study of the Interconversion between HCO (formyl) and COH Surface Reaction Intermediate on Pt(111)**, ***L. Arnadottir***, *E.M. Stuve,* University of Washington, *H. Jónsson*, University of Iceland

Two forms of the reaction intermediate with H:C:O stoichiometry were studied on Pt(111) using density functional theory. Three cases were studied: the intermediate on a clean surface, the intermediate and one water molecule on the surface and the intermediate with a water bilayer. Both the H-C=O (formyl) and C-OH configurations were found to be stable on clean Pt(111) and when coadsorbed with a water molecule. Interconversion between the two configurations was studied using the nudged elastic band method. On the clean surface interconversion between the two forms goes through a CO_{ads} and H_{ads} intermediate, meaning that although both HCO and COH are stable on the clean surface they will not interconvert. In the presence of coadsorbed water molecule the activation barrier for the interconversion from HCO to COH was found to be 0.62 eV. While the HCO configuration is stable in the presence of a water bilayer, the COH configuration dissociates to CO_{ads} and H_{ads}. These results suggest that, in the presence of water, the HCO form will be the only stable form of the reaction intermediate of H:C:O stoichiometry.

10:40am **SS1-TuM9 Enantioselectivity and Structure of Naturally Chiral Metal Surfaces**, ***A.J. Gellman***, *Y. Huang, L. Baker*, Carnegie Mellon University

The high Miller index surfaces of single crystal metals have chiral structures and have been shown to interact enantiospecifically with chiral adsorbates. There are many demonstrations of this phenomenon originating from several laboratories around the world. One specific example is the adsorption of R-3-methylcyclohexanone on $Cu(hkl)^{R\&S}$ surfaces. Several years ago we demonstrated that the adsorption of R-3-methylcyclohexanone on the $Cu(643)^{R\&S}$ surfaces was enantiospecific. The desorption energies of R-3-methylcyclohexanone adsorbed at R and S kinks differed and the orientation of the molecule at the R and S kinks differed. Over the past two years we have completed a study of the adsorption of R-3-methylcyclohexanone on a set of 16 single crystal surfaces spanning the entire stereographic projection. In spite of the complex variety of surface structures, we find that the adsorption sites on all surfaces can be classified as terraces, step and kink type sites and have adsorption energies for R-3-methylcyclohexanone that are quite distinct from one another. One of the important observations is that some of the nominally straight step edges such as those found on the Cu(410) surface exhibit behavior similar to that of the kinks on the Cu(643) surface. This arises because these (410) step edges are in fact quite rough and are not formed by close packed rows of atoms. Recent work has focused on the structure of chiral Cu surfaces. Molecular simulation by various other groups has demonstrated that the kinked step edges of these surfaces are roughened by annealing to high temperatures and that such step edges expose a variety of different kinks sites that are not found on the ideally terminated high Miller index surfaces. Scanning tunneling micrographs of these surfaces that have been reported by other groups bear out this description of the structure of the high Miller index surfaces. Over the past year we have developed the use of Xe TPD and Xe UV photoemission as a means of obtaining spectroscopic characterization of the kink step and terrace site densities on these surfaces.

11:00am **SS1-TuM10 Tunneling Contributions in β-Hydride Elimination of Ethyl Groups on Cu(111) and Cu(100) surfaces**, ***Y. Huang***, *A.J. Gellman, D. Sholl*, Carnegie Mellon University

Ethyl groups decompose into ethylene through the β-hydride elimination on Cu(111) and Cu(100) single crystal surfaces. Density Functional Theory calculations for β-hydride elimination of ethyl groups on Cu(111) and Cu(100) have been conducted by Sholl et al. These calculations suggested that hydrogen tunneling influences the kinetics of β-hydride elimination of ethyl groups on Cu(111) but not on Cu(100). Based on the calculations the Deuterium isotope effect in β-hydride elimination of ethyl groups should be greater on Cu(111) than on Cu(100). To verify this temperature programmed desorption (TPD) spectra of ethyl iodide and ethyl-2,2,2-d_3 iodide on both Cu(111) and Cu(100) were obtained. The pre-exponential and activation barrier to β-hydride elimination reactions were determined and compared on both Cu(111) and Cu(100) surfaces.

11:20am **SS1-TuM11 CO Chemisorption on Cu(111) via Embedded Configuration Interaction Theory**, ***S. Sharifzadeh***, *P. Huang, E.A. Carter*, Princeton University

Although density functional theory (DFT) is often considered the electronic structure method of choice to study surfaces, situations exist where DFT fails, e.g. strongly correlated electrons and descriptions of unoccupied states. As an example, CO adsorption on Cu(111) is poorly described within DFT because the CO bond to Cu(111) involves Cu back-donation to the empty CO 2pi* orbitals, which are at too low an energy in DFT, leading to an overestimation of pi back-bonding. Measurements at low coverage are consistent with on-top site CO adsorption on Cu(111), whereas pseudopotential-based DFT methods predict hollow site adsorption, due to the overestimation of the importance of pi-back-bonding. In this work, we study CO/Cu(111) with a density-based embedding strategy, where a local region of interest, described by accurate ab initio quantum chemistry calculations, is embedded into a background described by DFT. The region of interest is represented by a cluster of atoms that includes CO and nearby metal atoms. A self-consistent, DFT-based embedding potential accounts for the effect of the background on this cluster. Since ab initio quantum chemistry methods, e.g. configuration interaction (CI), give a better description of the CO LUMO, we expect an improvement on the description of CO chemisorption. We will present site preferences and adsorption energies from embedded CI, as well as comparing to periodic DFT and finite cluster calculations.

11:40am **SS1-TuM12 Mechanistic Insights Into Methane Activation from State-Resolved Beam-Surface Scattering Measurements**, ***A.L. Utz***, *D.R. Killelea, V.L. Campbell, D.F. Del Sesto, N.S. Shuman*, Tufts University

State-resolved surface scattering experiments provide detailed insight into the mechanistic basis for methane activation. We use infrared laser excitation of molecules in a supersonic molecular beam to prepare reagents with a well-defined internal and translational energy. The state-resolved reaction probabilities that we measure reveal which molecular motions (methane stretching and bending, translation, and surface atom motion) best promote reaction. Earlier work in our lab has shown that on Ni(111), C-H stretching excitation is significantly more effective than translational energy or bending excitation in promoting methane dissociation. Recent measurements demonstrate our ability to exert bond-selective control over methane dissociation. We excite the C-H stretch in CHD_3 and detect exclusively reaction products from the C-H bond cleavage channel. In contrast, thermal excitation of CHD_3 vibrations leads to a preference for C-D bond cleavage. This observation contradicts statistical pictures of gas-surface activation and indicates that energy exchange during direct dissociation is not complete on the timescale of reaction. The presentation will highlight recent experimental results from our lab, discuss how these results teach us about the reaction coordinate for methane activation, and explore how limited energy flow during reaction impacts our understanding of the energetics of hydrocarbon activation.

12:00pm **SS1-TuM13 Preparation of Nickel Nanoparticles and their Catalytic Activity in the Cracking of Methane.**, ***J.C. De Jesus***, *I. Gonzalez*, PDVSA-Intevep, Venezuela, *M. Garcia, C. Urbina*, Universidad Central de Venezuela

In this study, a facile method for the preparation of nickel nanoparticles is employed to investigate the catalytic decomposition of methane into carbon nanotubes. Nickel acetate tetrahydrate decomposes readily below 350°C to form metallic nanoparticles (average size 10-80 nm), and weight changes measured inside a thermogravimetric analyzer (TGA) in methane streams can be related quantitatively to the production of carbon nanotubes by catalytic cracking. C to Ni atomic ratios (C/Ni) estimated directly from TGA data provided a systematic approach to study in-situ the catalytic activity of the nickel nanoparticles. Methane cracking starts at temperatures as low as 400°C and continues efficiently until approximately 600°C. Between 600°C and 660°C, methane decomposition momentarily breaks off, while presumably the catalytic system undergoes a self-reorganization. Cracking resumes at 660°C and continues slowly up to 950°C. The amount of carbon deposited in the 600-660°C interval shows a lineal dependence with methane concentrations, with C/Ni ratios ranging from 6 to 31. Transmission electron microscopy (TEM) images of the different C/Ni residues collected at 660°C showed that during cracking narrower carbon nanotubes are produced at elevated methane concentrations, suggesting dispersion of nickel nanoparticles.

Surface Science

Room: 611 - Session SS2-TuM

Surface Structure and Growth on Metals

Moderator: T. Risse, Fritz-Haber-Institut der MPG, Germany

8:00am **SS2-TuM1 Crystalline Structure of Sn/Cu(100) Across a Surface Phase Transition**, ***J. Martínez-Blanco***, *V. Joco*, Universidad Autónoma de Madrid, Spain, *C. Quirós*, Universidad de Oviedo, Spain, *P. Segovia, E.G. Michel*, Universidad Autónoma de Madrid, Spain

The crystalline structure of 0.5 monolayer of Sn atoms adsorbed on Cu{100} has been studied by surface X-ray diffraction (SXRD) measurements. This surface undergoes a temperature-induced phase transition at 360 K from a single domain ($\sqrt{2}$ x $\sqrt{2}$)R45° phase at high temperature to a two rotated domains ($3\sqrt{2}$ x $\sqrt{2}$)R45° phase at low temperature. In a previous work[1] this phase transition was identified as being due to the stabilization of a charge density wave (CDW), with gapping of nested regions of the high temperature Fermi surface in excellent agreement with the CDW periodicity. We performed temperature-dependent SXRD measurements in order to obtain information on the atomic displacements across the phase transition and to understand the nature of the two phases observed. A full data set including in-plane reflections, superstructure rods and crystal truncation rods was measured for each phase. The optimization method employed for fitting the experimental data for both the high and low temperature phases is a type of genetic algorithm called Differential Evolution,[2] used in this work for the first time to extract crystallographic information from SXRD data. For the low temperature phase, we compare the model obtained with a previous surface structure model.[3] Our results confirm the removing of every third row of copper in the alloyed top layer and a concomitant pairing of Sn atoms as the origin of the triple periodicity. However, we obtain slightly different values for the atomic displacements in deeper layers. For the high temperature phase, the overall dependence of the measured structure factors with the perpendicular momentum transfer is similar to the values extracted from the low temperature phase, suggesting a disordered nature for the high temperature phase. We propose a detailed model for this phase and for the nature of the thermal induced disorder. We discuss possible mechanisms to keep the local structure across the phase transition and the nature of the high temperature disordered phase.

[1] J. Martínez-Blanco et al., Physical Review B, 72 (2005), 041401(R)

[2] M. Wormington et al., Phil. Trans. Roy. Soc. London Sers A, 357 (1999), 2827-2848

[3] K. Pussi et al., Surface Science, 549 (2004), 24-30.

8:20am **SS2-TuM2 Self-assembled MnN Superstructure on Cu(001) Surface**, *X. Liu, B. Lu, T. Iimori*, ***K. Nakatsuji***, *F. Komori*, University of Tokyo, Japan

Recently, self-assembled nanostructures have attracted tremendous interest. Among them, the ones with regular spatial array, uniform and well-defined geometric and structural characters, are especially desirable. However, it is still difficult to prepare such high-quality nanostructures. In the present paper, we describe the fabrication of self-assembled manganese nitride nano-islands on the Cu(001) surface and propose a new mechanism of the nano-self-assembling.[1] Each island shows a square shape and has a well-defined size of 3 nm x 3 nm. They are regularly arranged with a periodicity of (3.5 ± 0.1) nm and form a two-dimensional square superstructure. The depth of the trench between the islands is the same as the step height of the surface or the height of the island on the superstructure. The nano-islands adopt a NaCl-like structure which is oriented in the same way as the fcc Cu(001) substrate. They are reproducibly prepared in three steps in ultrahigh vacuum by mono-atomic layer of Mn deposition, atomic nitrogen exposure to the saturation and gradual annealing up to 630 K. The stoichiometry of the manganese nitride islands has been studied by in-situ X-ray photoelectron spectroscopy. It is determined that the formula of the manganese nitride is MnN. This stoichiometry is the same as that of the bulk MnN crystal, which has a face-centered tetragonal structure (distorted NaCl structure) with a lattice constant lager than that of Cu(001).[2] Thus, the nanostructure formation is attributed to strain-relief at the interface. However, different from the conventional stress-domain dominated self-assembly, the shape, size, and periodicity of the MnN islands do not change even when they coexist with the clean Cu(001) surface. This indicates that the self-assembling is driven not by the long-range strain relief, but by a short-range mechanism.

[1] X. Liu, B. Lu, T. Iimori, K. Nakatsuji and F. Komori, Phys. Rev. Lett. 98, 066103 (2007).

[2] K. Suzuki, T. Keneko, H. Yoshida, Y. Obi, H. Fujimori, and H. Morita, J. Alloys Comp. 306, 66 (2000).

8:40am **SS2-TuM3 Surface Morphology and Step Fluctuations on Ag Nanowires**, ***C.G. Tao****, *W.G. Cullen, E.D. Williams,* The University of Maryland, College Park, *S.E. Hunyadi, C.J. Murphy*, The University of South Carolina

Semiconducting and metallic nanowires have been the subject of intense research efforts for their potential applications in nanoscale electrical circuits and chemical sensors. For all the applications, and especially for sensors, the morphological and thermodynamic nature of the nanowire surfaces, including the presence of defects like steps and twin boundaries, play a crucial role in the functional response. Even though there have been many demonstrations of nanowire applications, extremely few studies directly address the issues of cleanliness and structural morphology of the surfaces of nanowires at the atomic scale. Here we will present the surface morphology and thermodynamic properties of Ag nanowires, characterized by scanning tunneling microscopy (STM) at room temperature. The Ag nanowires were prepared via a seedless, surfactantless wet chemical synthesis process and suspended in water. They then are redispersed into methanol by centrifugation, and are deposited onto atomically clean Ag thin films in ultra-high vacuum via a solution deposition method. By gently annealing the samples, methanol on the substrate and the surfaces of Ag nanowires is removed. The STM topography images reveal the facets of the penta-tetrahedrally twinned crystals which constitute the Ag nanowires, and sawtooth features of the boundaries of neighboring twinned crystals. On the facets, frizzy monatomic steps and rectangular shapes monolayer islands are clearly observed. Using a dynamic STM scan method, we obtain quantitative properties of step fluctuations, which are governed by periphery diffusion. Combing previous density functional theory (DFT) calculations and dynamics studies on low-index faces of Ag, we propose that the side facets are Ag(100) surfaces. Related studies about the time evolution of the twin boundaries and how the surface defects are associated with the electrical current flowing through the nanowires will also be discussed. --Supported by the NSF MRSEC (DMR 05) at the University of Maryland.

9:00am **SS2-TuM4 Capture-Zone Scaling and Universal Fluctuation Phenomena**, ***T.L. Einstein***, University of Maryland, *A. Pimpinelli*, Univ. of Maryland & U. Blaise Pascal--Clermont 2, France

As one approaches the nanoscale, fluctuations play an ever more important role in the physics of systems. Universal aspects of fluctuations are thus an especially timely topic. The Wigner distribution from random matrix theory has successfully described a vast array of physical phenomena, from energy spacings between nuclear levels to conductance fluctuations in wires, as well correlations of stock prices, spaces between parked cars, and times between successive unscheduled buses. It is easy to use, having the simple, one-parameter form a s^β exp ($-bs^2$) [with a and b being constants assuring normalization and unit mean, and s the fluctuating variable divided by its mean]. Here we apply this approach to the long-standing problem of island-size distributions during growth. We consider the distribution of the areas of Voronoi polygons (proximity cells) around nucleation centers, i.e. the capture zones (CZ). Generalizations of the Wigner distribution (to allow more than the 3 values of β based on symmetry) account well for data generated in kinematic Monte Carlo studies by several groups, much as it did for terrace-width distributions (TWD) on vicinal surfaces. For CZ distributions we find $\beta = i + 1$, where i is the size of the critical nucleus. (In spatial dimension $d = 1$, $\beta = 2(i + 1)$.) We demonstrate excellent fits of numerical data for both $d = 1$ and $d = 2$. To clarify the underlying physics, we present a phenomenological derivation by constructing a Langevin equation similar to that used in accounting for the equilibration of TWDs; we discuss the competing forces that lead to the WD. Our expression also describes well experimental data for pentacene adsorption and for CZ distribution of growing quantum dots. We compare this analysis with others using less-well-motivated Gamma distributions or more complicated expressions.

Work at UMD supported by the MRSEC, NSF Grant DMR 05-20471. Visits to UMD by AP supported by a CNRS Travel Grant, and TLE partially supported by DOE CMSN grant DEFG0205ER46227.

9:20am **SS2-TuM5 Sulfur Adsorption on Ag(111): Self-Organization of Metal-Sulphur Complexes below 300K**, ***M. Shen***, Iowa State University, *D.-J. Liu, C.J. Jenks, J.W. Evans, P.A. Thiel*, Ames Laboratory - USDOE, Iowa State University

We have investigated the interaction of sulfur with Ag(111). Sulfur was deposited using an electrochemical evaporator, which generated gas-phase sulfur in the form of S_2. Sulfur coverage was measured with Auger electron spectroscopy.[1] Images from scanning tunneling microscopy (STM) showed different structures at temperatures between 135 and 300 K. Deposition at 135 K led to the formation of two-dimensional (2D) islands. After heating to 200 K, the surface exhibited a quasi-1D "dot-row" structure, in which each dot was about 0.7 nm in diameter. The dots were aligned in rows that were separated by distances ranging from about 1.6 to 5 nm. Cooling back to 135 K did not restore the initial 2D island structure, indicating that the 2D islands may consist of S_2 that dissociates irreversibly in the heating step. At 300 K, no ordered structures were visible, suggesting that the adsorbate becomes very mobile. The STM observations at 300 K and 200 K could be produced reversibly, pointing to a reversible phase transition below room temperature. Development of the dot-row structure at high S coverage was accompanied by pitting on the terraces, indicating participation of Ag. DFT calculations show that Ag_3S_3 is a candidate for the dots. This complex is analogous to a metal-sulfur complex that has been proposed to exist on Cu(111).[2]

[1] K. Schwaha, N.D. Spencer, R.M. Lambert, Surf. Sci., 81, 273 (1979).

[2] P.J. Feibelman, Phys. Rev. Lett., 85, 606 (2000).

9:40am **SS2-TuM6 Structure of the Al(100)-c(2x2)Ti Surface***, ***M. Kopczyk***, *W. Priyantha, H. Chen*, Montana State University, *D. Tonn*, Balwin-Wallace Collage, *R.J. Smith*, Montana State University, *D.S. Choi*, Kangwon National University, Korea, *G. Bozzolo*, Ohio Aerospace Institute

The atomic structure of sub-monolayer amounts of Ti deposited on the Al(100) surface at room temperature has been studied using low-energy electron diffraction (LEED) and low-energy ion-scattering spectroscopy (LEIS/ ISS). The Ti coverage was determined using Rutherford backscattering spectroscopy. From the symmetry of the observed c(2x2) LEED images we infer a structure which places the Ti atoms in every other Al unit cell. Analysis of the LEIS spectra, including both azimuth- and polar-angle scans, corroborates this hypothesis. This conclusion is relevant to recent studies of Ti as a catalyst in Na alinates presently being studied for their use in hydrogen storage applications important in fuel cell research.

*This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **SS2-TuM9 Hard Superconductivity in Soft Quantum Films**, ***H.H. Weitering***, University of Tennessee **INVITED**

Superconductivity is inevitably suppressed in reduced dimensionality. Questions of how thin superconducting wires or films can be before they lose their superconducting properties have important technological ramifications and go to the heart of understanding coherence and robustness of the superconducting state in quantum-confined geometries. In this talk, I will show how quantum confinement of itinerant electrons in a soft metal, Pb, can be exploited to stabilize superconductors with lateral dimensions of the order of a few millimeters and vertical dimensions of only a few atomic layers. These extremely thin superconductors show no indication of defect- or fluctuation-driven suppression of superconductivity and sustain enormous supercurrents of up to 10% of the theoretical depairing current density. Their magnetic hardness implies a superconducting critical state with strong vortex pinning that is attributed to quantum trapping of vortices. Our study paints a conceptually appealing, elegant picture of a model nanoscale superconductor with calculable critical state properties and surprisingly strong phase coherence. Finally, I will show how the quantum growth and superconductive properties of the films can be tailored by Fermi surface engineering, and I will discuss the possibility of multi-gap superconductivity in quantum-confined thin films. This work was done in collaboration with M.M. Ozer, J.R. Thompson, Yu Jia, and Z.Y. Zhang.

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* Morton S. Traum Award Finalist

11:20am **SS2-TuM11 Initial Bilayer-by-Bilayer Growth of Ag Islands on NiAl(110): DFT Analysis of underlying Quantum Size Effects,** ***Y. Han****, D.-J. Liu, B. Unal, F. Qin, C.J. Jenks, J.W. Evans, P.A. Thiel*, Iowa State University

Growth of Ag on NiAl(110) is distinguished by an almost perfect match of the lateral unit cell of the substrate to that of Ag(110). Thus, Ag/NiAl(110) provides an ideal system in which to study morphological evolution during heteroepitaxy in the absence of lateral mismatch strain. Our STM studies reveal the nucleation and growth of large rectangular Ag islands for deposition of submonolayer amounts of Ag between 130K and 300K. Subsequent deposition produces smooth growth with large rectangular islands forming on top of coalesced clusters of such lower layer islands. However, the step height for the first layer islands is ~0.33 nm, and only slightly lower at ~0.29 nm for the next two layers. These values far exceed the step height of ~0.15 nm for Ag islands on Ag(110). Thus, we propose that islands have a predominantly bilayer Ag(110) structure for the first three (bi-) layers. This claim is supported by DFT calculations which reveal step heights for this structure in close agreement with experiment, and also indicate that the driving force for this bilayer growth is the presence of a quantum size effect perpendicular to the surface plane for electrons confined in the Ag film. Specifically, there is a strong oscillation of period 2 monolayers (ML) in the surface energy, and also in the binding energy of single Ag atoms on top of flat Ag films, favoring film heights equal to an even number of monolayers. For thicker films, step heights decrease so film structure must deviate from the perfect Ag(110) bilayer structure (a feature also reflected in a weak height modulation across the tops of Ag islands).

11:40am **SS2-TuM12 Role of Surface Structure on Thin Film Nucleation on Quasicrystal Surfaces,** ***B. Unal*****, Ames Lab., Iowa State Univ., *V. Fournee,* CNRS-UMR7584, France, *K.J. Schnitzenbaumer, C. Ghosh,* Iowa State Univ., *C.J. Jenks,* Ames Lab., Iowa State Univ., *A.R. Ross,* Iowa State Univ., *T.A. Lograsso,* Ames Lab., Iowa State Univ., *J.W. Evans,* Iowa State Univ., *P.A. Thiel*, Ames Lab., Iowa State Univ.

Quasicrystals are non-periodic but well-ordered solids. Their unusual atomic structures foster peculiar surface properties such as low friction and enhanced oxidation resistance. Using scanning tunneling microscope (STM) we have investigated clean surfaces of icosahedral (i) Al-Pd-Mn quasicrystals. By analyzing bulk structural models of i-Al-Pd-Mn quasicrystals, we suggest a relationship between the terminating layers and the clusters that form the basic building blocks of quasicrystals. Using STM, we have also investigated the nucleation and growth of Ag islands on the fivefold surface of an i-Al-Pd-Mn quasicrystal. The temperature dependence of island density suggests that trap sites control nucleation of Ag islands. We identify these trap sites as the cut clusters in the aforementioned structure analysis. Furthermore, we have developed a mean field rate equation model to explain this behavior. Our model suggests that the binding energy between Ag atoms at traps are significantly higher than that of Ag at regular terrace sites and the size of critical clusters is larger than one. This model will allow (qualitative) manipulation of experimental parameters to tailor island characteristic on quasicrystal surfaces.

12:00pm **SS2-TuM13 A Photoelectron Diffraction Study of $Cu_3Mn(100)$,** ***J. King-Lacroix****, N. Loh, D.-H. Yu, A.P.J. Stampfl,* Australian Nuclear Sci. and Tech. Org., *H. Ruppender, H. Over,* Justus-Liebig-Univ. Gießen, Germany, *E. Huwald, J.D. Riley,* La Trobe Univ., Australia, *A. Smith,* Monash Univ., Australia, *L.-J. Fan, Y.-W. Yang*, National Synchrotron Radiation Res. Ctr., Taiwan

In the Angstrom to nanoscale regime where electronic localisation blurs to itinerant behaviour, magnetic phenomena become highly dependent on dimensionality and local environment. Magnetic exchange between two different magnetic phases is one such phenomenon that is affected when dimensions are reduced to the nanoscale. We are specifically interested in studying the exchange properties at the interface of an antiferromagnetic or ferromagnetic material and a spin glass surface. Our first task however is to fully understand a spin-glass surface by mapping out the surface and bulk band structure as well as determine the surface crystalline structure. We have chosen the CuMn system because it represents a model spin-glass whose transition temperature is easily attainable. The bulk phase-diagram for the CuMn system displays a face-centered-cubic phase at room temperature for atomic percent concentrations of Mn from 0 to ~25% and the spin-glass transition temperature for CuMn in this percentage region increases linearly to ~110K at 25%at. Mn. We present here synchrotron-based azimuthal-scanned photoelectron diffraction measurements using the Cu and Mn 3p-orbitals from a $Cu_3Mn(100)$ surface and compare them to simulation and to corresponding data sets for Cu(100). The number of Mn-atoms in the upper-most layer is lower than expected from a truncated bulk surface suggesting surface segregation or oscillatory behaviour. Details of surface reconstruction and near-surface relaxation will be presented.

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* Morton S. Traum Award Finalist

Surface Science

Room: 608 - Session SS1-TuA

Bimetallics and Alloys

Moderator: I. Chorkendorff, Technical University of Denmark

1:40pm **SS1-TuA1 Atomic-Scale Assembly of a Heterogeneous Catalytic Site**, *P. Han,* Texas A&M University, *I. Lyubinetsky,* Pacific Northwest National Laboratory, ***D.W. Goodman***, Texas A&M University

The distance between surface Pd atoms is known to control the catalytic formation of vinyl acetate from ethylene and acetic acid by AuPd catalysts. In this study, we use the thermodynamic properties and the surface lattice spacing of a AuPd(100) alloy single crystal model catalyst to control and optimize the number of Pd monomer-pair sites with a specific Pd-Pd distance. Scanning tunneling microscopy reveals that sample annealing has a direct effect on the surface Pd arrangements: short-range order preferentially forms Pd-pairs located at local c(2 x 2) sites, sites known to be active for vinyl acetate synthesis. This methodology should be useful in the optimization of bimetallic industrial catalysts.

2:00pm **SS1-TuA2 Mechanistic Studies of the Steam Reforming of Methanol on PdZn Alloy Catalysts**, *E. Jeroro,* ***J.M. Vohs***, University of Pennsylvania

Methanol and other alcohols are potential bio-renewable sources of hydrogen. The use of alcohols, however, as a H2 source or storage medium requires stable reforming catalysts that have high activity and selectivity at low temperatures. One such catalyst that has received much attention for steam reforming of CH_3OH (SRM) [$CH_3OH + H_2O$? $CO_2 + 3H_2$] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity (>95%) for the production of CO_2 and H_2 from methanol, in spite of the fact that bulk Pd exhibits nearly 100 % selectivity for the dehydrogenation of CH_3OH to CO and H_2 under typical SRM conditions. While it has been demonstrated that formation of a PdZn allow is required to obtain high selectivity, the mechanism by which Zn alters the reactivity of the Pd is not understood. In this talk we will present results of a study of model PdZn catalysts consisting of submonolayer amounts of Zn supported on Pd(111) that provide insight into the synergistic interactions between Zn and Pd and how they alter the reactivity of the Pd surface. Temperature programmed desorption (TPD) data for the reaction of methanol, formaldehyde and carbon monoxide on Pd(111) as a function of Zn coverage as well as results of a high resolution electron energy loss spectroscopy (HREELS) study of the bonding configurations of these molecules on Zn/Pd(111) surfaces will be presented. The TPD data show that the formation of the PdZn alloy significantly decreases the activity of the Pd surface for the dehydrogenation of CH_3OH and CH_2O. This change in reactivity is found to be due in part to a change in the bonding configuration of adsorbed formaldehyde intermediates. The experimental results also provide evidence for a strong electronic interaction between the Pd and Zn which affects the adsorption energies of CO and methanol.

2:20pm **SS1-TuA3 Revisiting the CO oxidation on a Au/Ni(111) Surface Alloy**, ***J. Knudsen***, *L.R. Merte, R.T. Vang,* University of Aarhus, Denmark, *A. Resta, J. Schnadt, J.N. Andersen,* Lund University, Sweden, *F. Besenbacher*, University of Aarhus, Denmark

In the early 1990s our group showed that deposition of gold onto nickel single-crystal surfaces results in the formation of a stable alloy in the crystal's topmost layer, a surprising discovery considering that the two metals are immiscible in the bulk. This surface alloy was later shown to display interesting catalytic properties; for example, the presence of small amounts of gold in nickel catalysts hinders graphite formation during steam reforming of hydrocarbons.[1] Other studies explored the use of gold to inhibit CO dissociation on Ni(111) and the stability of the surface alloy under high-pressure conditions.[2] Most recently, Lahr and Ceyer reported that the Au/Ni(111) surface alloy catalyzes oxidation of CO to CO_2 at temperatures as low as 70K.[3] They conclude that gold atoms substituted into the top layer of the Ni(111) surface stabilize chemisorption of a reactive, non-dissociated O_2 species in a similar manner as has been reported for gold nanoclusters. We have used scanning tunnelling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to study the adsorption, coadsorption and reaction of CO and O_2 on the Au/Ni(111) surface alloy and the clean Ni(111) surface with the goal of clarifying the mechanism or mechanisms behind this interesting phenomenon. In agreement with the work of Lahr and Ceyer we find that molecular oxygen is required to produce CO_2 on the surface but our results seem to indicate a different reaction mechanism than the one proposed in their article.

[1] Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Norskov, J. K.; Stensgaard, I., Design of a surface alloy catalyst for steam reforming. Science 1998, 279, (5358), 1913-1915.

[2] Vestergaard, E. K.; Vang, R. T.; Knudsen, J.; Pedersen, T. M.; An, T.; Laegsgaard, E.; Stensgaard, I.; Hammer, B.; Besenbacher, F., Adsorbate-induced alloy phase separation: A direct view by high-pressure scanning tunneling microscopy. Physical Review Letters 2005, 95, (12), 126101.

[3] Lahr, D. L.; Ceyer, S. T., Catalyzed CO oxidation at 70 K on an extended Au/Ni surface alloy. Journal Of The American Chemical Society 2006, 128, (6), 1800-1801.

2:40pm **SS1-TuA4 General Trends in the Electronic and Chemical Properties of Monolayer Bimetallic Surfaces**, ***J.G. Chen***, University of Delaware **INVITED**

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. The modification effect is especially important at the admetal coverages in the submonolayer and monolayer regime. However, it is difficult to know a priori how the chemical properties of a particular bimetallic surface will be modified relative to the parent metals. We have investigated the electronic and chemical properties of model bimetallic surface structures, in particular subsurface and surface monolayers, using a combination of experimental and theoretical modeling to gain further insights into these factors. In the current presentation we will first utilize the adsorption and desorption of hydrogen to demonstrate the correlation between the hydrogen binding energy and the center of the surface d-band in various bimetallic surfaces. We will also provide a general equation that allows one to predict how the electronic properties, especially the d-band center, will be affected in bimetallic systems. We will then use several probe reactions, including hydrogenation of alkenes and reforming of oxygenates, to show the correlation between the chemical activities and the surface d-band center of bimetallic surfaces. Finally, we will discuss the relative stability of surface and subsurface bimetallic structures in vacuum, and in the presence of adsorbed hydrogen and oxygen.

4:00pm **SS1-TuA8 Real-time STM Observations of the Oxidation of a Ti/Pt(111)-(2x2) Surface Alloy using O_2 and NO_2**, *S. Hsieh,* National Sun Yat-Sen University, Taiwan, *G. Liu,* ***B.E. Koel***, Lehigh University

We have used scanning tunneling microscopy (STM), low energy diffraction (LEED), and Auger electron spectroscopy (AES) to study the nascent oxidation of an ordered Ti/Pt(111)-(2x2) surface alloy exposed to oxygen (O_2) or nitrogen dioxide (NO_2) under ultrahigh vacuum conditions. The Ti/Pt(111)-(2x2) surface alloy was formed by depositing an ultrathin Ti film on Pt(111) and annealing to 1050 K. This produces an alloy film in which the surface layer is pure Pt and the second layer contains Ti atoms in a (2x2) structure that causes the pattern observed by STM and LEED. Real-time imaging of the surface at 300 K was carried out by continuously scanning with the STM while either O_2 or NO_2 was introduced into the chamber. O_2 exposures did not cause any gross structural changes, however oxygen was detected on the surface afterwards using AES. Annealing this surface to 950 K resulted in the formation of an ordered TiO_x overlayer as characterized by both LEED and STM. In contrast, NO_2 exposures caused definite changes in the surface morphology at 300 K, and the RMS roughness increased from 3.5 to 7.1 Å after a 93-L NO_2 exposure. No ordered structures were produced by this exposure, but annealing the surface to 950 K formed an ordered pattern in LEED and corresponding clear, well-resolved structures in STM images. Disruption or reconstruction of the Ti/Pt(111)-(2x2) surface alloy because of Ti oxidation is an activated process. The energetic barrier to TiO_x formation can not be surmounted at room temperature at low oxygen coverages and annealing the surface was necessary to initiate this reaction. However, the higher oxygen coverages obtained using the more reactive oxidant NO_2 lowered the chemical potential in the system sufficiently to overcome the activation barrier to extract Ti from the alloy and form a disordered TiO_x film at room temperature. These results illustrate the importance of the surface oxygen coverage in nucleating the room temperature oxidation of the Ti/Pt(111)-(2x2) surface alloy.

4:20pm **SS1-TuA9 CO Tolerance of Pt Islets on Ru(1000) and their Implications for PtRu Nanocatalysts: Insights from First Principles Calculations**, ***T. Rahman***, *S. Stolbov, M. Alcantara-Ortigoza*, University of Central Florida

Proton exchange fuel cells are promising tools for hydrogen economy. However, CO traces which are inevitably present, block active sites of the Pt anode and hence poison its reactivity. Recently, Ru nanoparticles with submonolayer Pt coverage are found[1] to be much more tolerant to CO than commercial catalysts. To understand the rationale for this tolerance, we have performed density functional theory based calculations of the energetics of adsorption and diffusion of CO on Pt islets on Ru(0001). We find that the total energy of the system gradually decreases as the CO molecule moves from the center of the islets to its edge and further onto substrate. Diffusion barriers for CO are found to be low: 0.06 eV to move from the center of the island to its edge, 0.27 eV to "jump" from the Pt island edge to a neighboring substrate site, and 0.3 eV to move further along the Ru surface. Assuming the pre-factor of CO diffusion to be 1012 sec-1, the diffusion rate at the operating temperature 350K is estimated to be around 107 sec-1. These results suggest that this catalyst is CO tolerant because of the propensity of CO to move from active Pt island site to the Ru substrate. We trace this effect to the features of the local densities of electronic states around the Fermi-level.

[1] S. R. Brankovic, J. X. Wang, and R. R. Adžic, Electrochem. Solid State Lett.4, A217 (2001).

[2] Work supported in part by DOE-BES under grant DE-FG02-07ER15842.

4:40pm **SS1-TuA10 Effect of Quantum Well States on Adsorption of CO Molecules**, ***W. Kim***, *S. Han, D. Lee, C. Hwang,* Korea Research Institute of Standards and Science, *C. Min,* Seoul National University, Republic of Korea, *H. Lee, H. Kim*, Pohang Accelarator Laboratory, Republic of Korea

Formation of quantum well states in the metallic thin film systems satisfying specific boundary conditions leads to the oscillation of the electron density of states at Fermi level as the thickness of the film increases.[1] We investigated the effect of the oscillation on adsorption of CO molecules in case of the Cu/Co/Cu(100) system. The quantum well states and resulting oscillation of density of states at Fermi level in wedge-shaped Cu/Co/Cu(100) system were confirmed by angle-resolved photoemission spectroscopy. After adsorption of CO molecules at the substrate temperature of 100 K, we observed the shift of binding energies of quantum well states, which could be understood in the scheme of phase accumulation model. C 1s core level photoemission spectra of the adsorbed molecules were measured as a function of temperature for each Cu thickness. The initial feature of the C 1s spectra show well-known three peak structure similar to that of CO molecules adsorbed on Cu(100). From the temperature dependence of the intensity of measured C 1s core level spectra, we could determine the desorption temperature of CO molecules for each Cu thickness, which showed clear dependence on the density of states of Fermi level with oscillating variation of 15 K. We also evaluated the relative ratio of the first satellite peak to main peak in C 1s core level spectra and found out that the ratio showed oscillatory behavior and strong correlation with the density of states at Fermi level. Our observations confirm the old theoretical explanation on the origin of three peak structure of C 1s core level spectra of CO molecules adsorbed on the Cu(100) surface.[2]

[1] Z. Q. Qiu and N. V. Smith, J. Phys.: Condens. Matter vol.14, R169.

[2] O. Gunnarsson, and K. Schöhammer, Phys. Rev. Lett. vol 41, 1608.

5:00pm **SS1-TuA11 Modifying the Adsorption of Molecules at Metal Surfaces by Quantum Confinement of Electrons**, ***L. Tskipuri***, *R.A. Bartynski*, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. Quantum confinement of electrons forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we found that MQW states modify the strength of CO bonding to Cu MQW overlayers on the pseudomorphic fcc-Co/Cu(100) and fcc-Fe/Cu(100) systems.[1] In these systems, the CO-metal bond strength oscillates, in correlation with MQW states, as a function of Cu overlayer thickness. Here we extend these studies with IR studies of CO adsorbed on Cu MQWs and report on the adsorption properties of the pseudomorphic transition metal layers themselves. These systems have partially filled d-bands may be grown in a metastable structure. We have examined the unoccupied electronic structure and CO bonding strength on the n-ML fccNi/Cu(100) and n-ML fccCo/Cu(100) systems using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). In the case of Co, the as-grown films exhibit well-defined unoccupied MQW states, but they do not cross the Fermi level. This allows us to investigate adsorbate-MQW interactions that involve MQW states away from the Fermi level. Upon CO adsorption a well-defined structure centered about 3.8 eV above the Fermi level appears and is assigned to the unoccupied CO 2π orbital. CO adsorbs molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 375 K, which is about 30 K lower than what is observed for CO adsorbed on the hcp Co surfaces. When Co films are dosed at low temperatures (~ 100K), we find a second CO desorption peak around 230 K, once again similar to what is seen for hcp Co, but as a markedly lower temperature. These peak desorption temperatures change as a function of film thickness and are correlated with two different C-O stretch vibrational frequencies observed in the IR spectra. We have observed similar desorption peak temperature shifts when CO desorption from the Ni/Cu(100) system as a function of thickness and as compared to single crystal Ni(100). The role of quantum confinement and surface strain in producing the observed effects will be discussed.

[1] A. G. Danese, F. G. Curti, and R. A. Bartynski, Phys. Rev. B 70, 165420 (2004).

Surface Science

Room: 611 - Session SS2-TuA

Excitations at Surfaces

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

2:00pm **SS2-TuA2 Electronic Excitation and Bond Dissociation via Transient Anion Formation at the Surfaces of Molecular and Biomolecular Solids**, ***L. Sanche***, University of Sherbrooke, Canada **INVITED**

Electrons with energies in the range 0-30 eV can induce at interfaces and surfaces specific reactions which are relevant to applied fields such as nanolithography, dielectric aging, radiation waste management, radiation processing, astrobiology, planetary and atmospheric chemistry, surface photochemistry, radiobiology, radiotherapy and ballistic electronics. The action of low energy electrons (LEE) at the surface of molecular and biomolecular solids has been investigated with model systems consisting of pure or doped thin molecular films. Some of the results will be presented at the conference. In these experiments a target film is deposited on a metal or semi-conductor substrate and bombarded by a LEE beam under ultra high vacuum (UHV) conditions. Backscattered electrons are energy analysed to determine the energy and characteristics of electronic excited states at the surface of the molecular solid. Bond dissociation is analysed by mass spectrometry (MS); i.e., we determine the energy, mass and intensity of the neutral fragments and ions emanating from the films vs electron energy. The products remaining in the films are analyzed in situ by X-ray photoelectron and electron energy loss spectroscopies; they can also be removed from the UHV system and analyzed by HPLC and LC/MS. By comparing the results of the theory and different experiments, it is possible to determine fundamental mechanisms that are involved in the processes induced by LEE. Such mechanisms involve the formation of transient anions which play a dominant role in the fragmentation of all molecules investigated and dipolar dissociation which produces an anion and a cation. The transient anions fragment the parent molecules by decaying into dissociative electronically excited states or by dissociating into a stable anion and a neutral radical. These fragments usually initiate other reactions with nearby molecules, causing further chemical damage. The damage caused by transient anions is dependent on the molecular environment. This research is financed by the CIHR.

2:40pm **SS2-TuA4 An Atomic Seesaw Switch by Tunneling Carrier Injection on Ge (001)**, ***K. Tomatsu***, *K. Nakatsuji, T. Iimori,* University of Tokyo, Japan, *Y. Takagi,* Riken Harima, Japan, *H. Kusuhara, A. Ishii*, Tottori University, Japan, *F. Komori*, University of Tokyo, Japan

Reversible switching of electronic conduction through atom manipulation is one of the main subjects of nanoscience. However, different conducting pathways have not been clearly observed with atomic resolution. Here, we demonstrate the correlation between the change of surface atomic position by tunneling carrier injection and that of the reflection of one-dimensional (1D) surface-state electrons on the Ge (001) surface with a low density of heterogeneous Sn-Ge dimers.[1] On the clean Ge(001) surface, two atoms form a buckled dimer, and bonding π- and antibonding π^*-states localize on upper and lower atoms of the dimer. The Ge dimers align in the [110] direction and form a dimer row. The π^*-electron behaves like a 1D free electron along the dimer row. It has been shown that the buckling orientation of the Ge dimer can be reversibly controlled by surface bias voltage of STM.[2] This conformation change is induced by inelastic scattering of injected carriers from the STM tip to the surface under the electric field due to the bias voltage. When Sn atoms are deposited on the clean Ge(001) surface at room temperature, buckled dimers originating from the Sn atoms are formed at the Ge dimer position in the surface.[3] We identify the dimer as a heterogeneous Sn-Ge dimer by reversing its buckling orientation with STM and observing the change of the STM images at 80 K. An atomic seesaw switch is realized for the 1D π^* electrons in the Ge dimer-row direction by using the STM to reversibly flip the buckling orientation of a single Sn-Ge dimer in the dimer row. When the Sn atom of the heterogeneous dimer is at the lower position, the 1D electrons are reflected and a standing wave of this state is observed in the dI/dV image. Whereas, when it is at the upper position, the 1D electrons pass through the heterogeneous dimer, and no standing wave is observed. In this state, the lower atom of the dimer is Ge, and the π^* state of the dimer is little different from that of the Ge-Ge dimers. These are confirmed using first-principles calculations.

[1] K. Tomatsu, K. Nakatsuji, T. Iimori, Y. Takagi, H. Kusuhara, A. Ishii, F. Komori; Science 315, 1696, 2007.

[2] Y. Takagi, Y. Yoshimoto, K. Nakatsuji, F. Komori; Phys. Rev. B75, 115304, 2007.

[3] K. Tomatsu, K. Nakatsuji, T. Iimori, F. Komori; Surf. Sci. 601, 1736, 2007.

3:00pm **SS2-TuA5 Detection of Hydrogen During Low-Energy (5-50 eV) Electron Bombardment of Acetylene Adsorbed on Si(111) Surfaces**, ***K.R. Shepperd***, *T. Li, P.N. First, T.M. Orlando*, Georgia Institute of Technology

The interaction of hydrocarbons with Si surfaces is a topic of wide interest. This is generally related to the technological importance of SiC and the growing interest in graphene. In an effort to grow SiC interfaces and graphene overlayers, we have investigated the interaction of C_2H_2 (C_2D_2) with Si(111) surfaces and the low-energy electron-beam induced chemistry of this adsorbate-substrate system. We monitor the production and release of hydrogen using sensitive and selective resonance enhanced multiphoton ionization laser detection schemes. We have measured the threshold energy and the yield vs. incident electron energy. We discuss the structure in the yields vs. energy in terms of direct dissociative excitations and dissociative electron attachment. We also have investigated the remaining carbon deposit using Auger electron spectroscopy, scanning electron and scanning tunneling microscopy. Initial results indicate facile formation of SiC at low coverage but no clear signature of graphene.

4:00pm **SS2-TuA8 Mechanism of Negative Ion Formation during the Laser Ablation of Alkali Halides[1]**, ***J.T. Dickinson***, *K. Kimura, S.C. Langford*, Washington State University

Pulsed excimer laser radiation produces a variety of surface and near surface defects in the alkali halides that contribute to particle emission. Quadrupole mass spectrometry during pulsed 248-nm laser irradiation of cleaved LiF, NaCl, KCl, and KBr shows intense emissions of positive alkali ions at fluences well below the threshold for visible plume formation. We argue that these ions are emitted directly from surface defect sites when nearby electron traps are photoionized. In this work, we describe somewhat weaker emissions of negative alkali ions with kinetic energies similar to that of the positive ions. Measurements of induced charge on a metal sheet mounted behind a thin sample show that the surface develops a positive charge during the laser pulse. Thus the direct emission of negative ions at these low fluences is not expected. In previous work, we have shown that the cloud of positive alkali ions is accompanied by enough electrons to compensate much of the positive charge. These electrons are electrostatically confined to the ion distribution to produce a mixed charge cloud. Although these electrons are available for electron attachment processes, detailed measurements on KCl show no Cl^- at our level of sensitivity, despite the presence of the neutral Cl, with its high electron affinity. We attribute the lack of Cl^- to the absence of spatial overlap between neutral Cl and the charge cloud. Since the detected neutral K and Cl have similar velocity distributions, negative ion formation by electron attachment to neutral K desorbed directly from the surface is similarly difficult. These considerations suggest that K^- is formed by double electron attachment to K^+. Measurements of the total ion and electron emissions imply that the electron and ion densities immediately after the laser pulse are sufficient to account for the production of the observed negative alkali ions by collisional electron-ion and electron-neutral recombination. Although electron attachment is frequently observed among the products of ablation at high fluences, it is remarkable that the conditions required for double electron attachment are attained at the low fluences probed in this work. Further study of the behavior of charged emissions in this well-studied system is required to clarify how these conditions develop.

[1] This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

4:20pm **SS2-TuA9 Dissociative Attachment of Adsorbed Methyl Halides by Dielectric Layer Image State Electrons**, ***E.T. Jensen***, University of Northern British Columbia, Canada

We have studied the transfer of low-energy electrons through thin films of n-hexane (C_6H_{12}) on a Cu(110) substrate. The band structure of the thin n-hexane layers allows relatively long-lived image states to be formed at the hexane-vacuum interface.[1,2] In our experiments, these image states are occupied by sub-vacuum level photoelectrons from the Cu(110) substrate that are generated by a near-UV laser, and tunnel through the n-hexane film into the image states. These image state electrons can couple to the unoccupied electron affinity levels of coadsorbed CH_3X (X=Br, I). Dissociative electron attachment (DEA) of the CH_3X is detected by the fission of the C-X bond, with the CH_3 fragment escaping into the vacuum and subsequently detected by a quadrupole mass spectrometer. The intermediary role of the image states in this DEA process is determined from the coverage dependencies of the CH_3 fragment yields and the distinctive translational energy distribution of the CH_3- the image state electrons constitute a nearly monochromatic electron source for DEA of the CH_3X.

[1] M.W. Cole, Phys. Rev. B 3 (1971) 4418.

[2] K. Nagesha and L. Sanche, Phys. Rev. Lett. 81 (1998) 5892.

4:40pm **SS2-TuA10 Photo-induced Surface Functionalization of Carbon Surfaces: The Role of Photoelectron Ejection**, ***P.E. Colavita***, *B. Sun, K.-Y. Tse, R.J. Hamers*, University of Wisconsin-Madison

Carbon based materials are attractive for a wide range of applications, from biomaterials to fuel cells; however their effective use often requires controlling the surface chemistry to incorporate recognition moieties or reactive centers. The high stability of carbon also makes it a challenging material to functionalize; recently, the use of ultraviolet light (254 nm) to initiate functionalization of carbon surfaces has emerged as a way to obtain carbon/organic interfaces with tailored properties. We have investigated the mechanism of covalent grafting of amorphous carbon surfaces with functional organic molecules using the photochemical reaction of terminal alkenes. Measurements comparing the reactivity of different n-alkenes bearing different terminal groups at the terminus opposite the olefin showed pronounced differences in reactivity. We characterized the rate and final coverage of the resulting organic layers using X-ray Photoelectron Spectroscopy (XPS) and Infrared Reflection Absorption Spectroscopy (IRRAS). Ultraviolet Photoelectron Spectroscopy (UPS) and photocurrent measurements suggested that the reaction involves photoelectron emission from the carbon surface into the liquid phase. Density functional calculations show a strong correlation between the electron affinity of the alkenes and the observed reactivity. The specific terminal group opposite to the olefin was found to play an important role in the stabilization of excess negative charges on the molecule, thus explaining the strong dependence of reactivity on the particular terminal group. These findings suggest that the reaction involves injection of photoelectrons into the alkene acceptor levels, leading to the formation of radical anions in the liquid phase. Finally, we demonstrate that the grafting of marginally reactive alkenes can be enhanced by seeding the surface with a small amount of good electron accepting groups. These results provide fundamental new insights into the role of electronic excitations in controlling rates and mechanisms of olefin reactions at surfaces. While demonstrated here for amorphous carbon, these results may also be significant for the UV initiated grafting of olefins on other semiconductors.

5:00pm **SS2-TuA11 Electron Stimulated Reactions in Thin Water Films Adsorbed on TiO_2(110)**, ***N.G. Petrik***, Pacific Northwest National Laboratory, *C.D. Lane, T.M. Orlando,* Georgia Institute of Technology, *G.A. Kimmel*, Pacific Northwest National Laboratory

The electron-stimulated desorption of molecular water from TiO_2 (110) surface was investigated as function of coverage (0-5 ML), incident electron energy (5-100 eV), and other parameters. The two main water adsorption sites - 5-fold coordinated Ti^{4+} ions and bridge-bonded oxygens (BBO)- have significantly different cross-sections for electron-stimulated desorption, but similar cross-sections for electron-stimulated dissociation. Isotopic layering experiments show that both desorption and dissociation of water adsorbed on the Ti^{4+} sites is suppressed by deposition of water molecules on the BBO sites. The results suggest that electronic excitations in water molecules adsorbed on the Ti^{4+} sites can produce reactions (desorption or dissociation) in water molecules on the BBO sites. The experimental observations are discussed in terms of specific structural characteristics of thin water films on TiO_2 (110).

Surface Science

Room: 4C - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Size-Selected Deposition of $Mo_6S_8^+$ on Au(111), ***M.J. Patterson***, Stony Brook University, *M.G. White*, Brookhaven National Laboratory

Nanoscale MoS_2 has a layered assembly that shows a high propensity towards folding, forming hollow nanotube and fullerene structures which display a wide range of catalytic, photovoltaic, and lubricant properties.[1-3] Supported MoS_2 nanoparticles are known for their ability to catalyze a wide array of heterogenous reactions, in particular hydrodesulfurization (HDS).[4-5] However, understanding the role of size, structure, and overall composition of the MoS_2 particles in HDS has not yet been resolved due to the inhomogeneity of these commercial catalysts. Work done in our laboratory is geared towards preparing homogenous samples in ultra high vacuum (UHV) that can serve as model systems for these types of catalytic reactions. We are currently investigating the reactivity of size-selected transition metal clusters generated in the gas-phase and deposited on a Au(111) surface. Using a magnetron cluster source, we are able to produce a wide range of nanoparticle stoichiometries including the metal sulfide core of the superconducting Chevrel phase[6], $Mo_6S_8^+$. The work presented here focuses on characterization of the $Mo_6S_8^+$ cluster deposited on a Au(111) single crystal using surface science techniques such as TPD, AES, XPS, and UPS.

[1] Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonfer, M.; Cohen, S. R.; Tenne, R. Nature 1997, 387, 791.

[2] Thurston, T. R.; Wilcoxon, J. P. Journal of Physical Chemistry B 1998, 103, 11.

[3] Chhowalla, M.; Amaratunga, G. A. J. Nature 2000, 407, 164.

[4] Topsoe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis; Springer: New York, 1996.

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SS-TuP2 Preparation and Characterization of Au Nanoparticle, ***G. Kutluk***, Hiroshima University, Japan, *S. Yagi*, Nagoya University, Japan, *H. Sumida*, Mazda Motor Co., Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

Gold highly dispersed on metal oxide supports has unexpectedly been found to be highly active for a number of catalytic reactions. However, the electronic nature of the gold species in active catalysts has not been fully elucidated. We have applied a modified version of the gas phase condensation combined with Arc plasma method for the metal nanoparticle synthesis. Which is not only convenient in synthesizing highly dispersive metal nanoparticle with cleaner surface but also is suitable for the size controlling. In addition, this method also shows advantage in synthesizing metal nanoparticle with simple shape on a supporting material (Si Ta, TaN). The performance of the gas phase condensation and Arc plasma method for the size control has been confirmed in the earlier work.[1] In this study, we report the investigations of the thermal stabilities, crystallographic structure and the size dependence of electronic structures of Au nanoparticle in range of 1.5 ~ 5nm in diameter. The Au nanoparticle were characterized by the TEM, AFM, XPS and UPS. Drastic change have observed in the 4f level photoemission spectrum when the size of Au particle down to 1.5nm. The spectrum is characterized by component of an oxidized doublet states of Au_2O_3 coexisting with the doublet states of pure Au. The vanishing of component of Au_2O_3 doublets has been observed with increasing the annealing temperature of the sample in the reduction atmosphere.

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SS-TuP3 Surface Reaction of $(CH_3S)_2$ /Rh(100) Depending on Adsorption Coverage Studied by XPS and NEXAFS, ***O. Sumi***, *T. Nomoto, S. Yagi, K. Soda,* Nagoya University, Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

The automobile exhaust catalysts oxidize and/or reduce the exhaust gases, such as CO, C_xH_y and NO_x. As know as Sulfur Poisoning, the sulfur-containing molecules that originate from fuels affect the reactivity of noble metals (Rh, Pt and Pd), which are capital components of the catalysts. There are some reports that Rh has the highest resistance to the Sulfur Poisoning among those noble metals. However there are a few reports that have an interest in adsorption reaction of sulfur-containing molecules at low temperature. Therefore it is important to investigate the reaction mechanism. In this report, we reveal the surface reaction of dimethyl disulfide (DMDS) on the Rh(100) surface using XPS and NEXAFS techniques. The clean Rh(100) single crystal was cooled down to 90 K and subsequently exposed to DMDS. DMDS coverage was controlled to 0.44 ML, 0.32 ML and multilayer. As a result of the XPS spectra at 0.44 ML, DMDS molecules are decomposed into methanethiolate and atomic S at 90 K. Methanethiolate is generated by the dissociation of S-S bond and partial methanthiolate dissociates into atomic S and methyl. After heating up to 170 K, XPS results indicate that some of methanethiolate desorbs. At 0.32 ML, DMDS molecules are also decomposed into methanethiolate and atomic S at 90 K. However the ratio of atomic S has increased and methanethiolate does not desorb but dissociates into atomic S at 170 K. These results indicate that the surface reaction depends on initial DMDS coverage. Polarization dependent S K-edge NEXAFS spectra for submonolayer at 90 K show that the peak intensity of σ^*(S-C) at 90° is larger than that of 20°. This results indicates that the coordination angle of σ^*(S-C) should be almost lying on Rh(100) surface.

SS-TuP4 XPS and NEXAFS Studies for Co-Adsorption Reaction of Dimethyl-Disulfide and Water on Rh(100), ***S. Yagi***, *O. Sumi, T. Nomoto, K. Soda*, Nagoya University, Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

It is an important reaction that water molecule plays some interaction in the bio-body. There are many sulfur-including molecules in the bio-body, such as L-cysteine amino acid. Is there any interaction between the sulfur-including molecule and water? We have pay attention to the interaction of the co-adsorption system, the sulfur-including molecule and water, on the transition metal surface. For the bio amino molecule of L-cysteine, it is reported that the L-cysteine molecule has an interaction with water molecule on transition metal surface.[1] For the adsorbate of L-cysteine on NI and Cu surfaces, the S-H bond dissociates and becomes thiolate form. It is found that the oo-adsorbed water molecule has a new bonding with the sulfur of the thiolate. Because the Sulfur K-edge Near-edge X-ray Absorption Fine Structure (NEXAFS) shows sigma*(S-O) peak at 2482 eV. It seems that there are bondings of three or four water molecules at the sulfur part of the thiolate. The adsorption systems of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) on Rh(100) surface have been investigated by T. Nomoto[2,3] and O. Sumi[4] by XPS and NEXAFS. For both adsorption systems, the adsorption molecules partly dissociates and becomes thiolate and atomic sulfur on the surface at 90 K. In this paper, the aim is to reveal the co-adsorption reaction of DMDS and water molecules on Rh(100) at 90 K by means of XPS and Sulfur K-edge NEXAFS techniques. Judging from the spectral results of XPS and NEXAFS, it is found that DMDS molecules partly dissociate and the adsorbates are the thiolate and atomic sulfur. In case of the co-adsorption with water, it is cleared that water molecule does not have an interaction with the atomic sulfur, but has a bonding with the thiolate.

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SS-TuP5 Illuminating Analysis of Observed Low-Dimensional Plasmons in an Array of Metallic Quantum Wires, ***T. Inaoka***, Iwate University, Japan, *T. Nagao*, National Inst. for Materials Sci., Japan

Using self-assembly of adsorbed Au atoms on vicinal surfaces of Si(111) with regular step rows, one can form a regular array of Au atom chains at interval of 1.91 nm on a Si(557) surface. Each atom chain of alternating Au and Si atoms embedded in the topmost Si layer of the terrace creates a one-dimensional (1D) surface-state band of metallic character. Conduction electrons in this band are confined in a narrow region one-atom wide. This array of metallic quantum wires sustains low-dimensional plasmons (PL's), namely, 1D PL's interacting with one another, and strong 1D confinement enhances the exchange-correlation (XC) effect on the PL's. In our previous work, by means of electron energy-loss spectroscopy (EELS) with a high wave-number resolution, we measured the low-dimensional PL's in the quantum-wire array.[1] In the present work, taking account of the interwire interaction and the XC effect, we investigate the dynamical response of the wire array to a probe electron in EELS. To consider the XC effect, we apply a self-consistent local-field-correction (LFC) theory to the wire array.[2] Although the interwire interaction is so significant as to produce a considerable distribution of the PL-mode energy, the calculated PL energy dispersion in EELS agrees with the dispersion of a single isolated wire. This paradox can be ascribed to the fact that the external potential generated by the probe electron is localized so sharply as to act and to produce substantial induced charges only on one or two wires. The calculated dispersion gives a complete explanation of the observed sound-wave character. By comparing the results of the LFC calculation with those of the Random-phase-approximation calculation, we evaluate the XC effect. This effect is found to operate to lower the PL energy and to heighten the energy-loss intensity in EELS. Our analysis can reproduce quantitatively the observed energy dispersion and energy-loss intensity.

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SS-TuP6 STM Study of Temperature Effect on Electron Induced Hopping Motion of CO/Cu(110), ***T. Okada***, The University of Tokyo, Japan, *S. Katano*, Tohoku University, Japan, *Y. Kim*, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Scanning tunneling microscope (STM) enabled the observation and manipulation of the single isolated molecule, and we can follow the molecular motion precisely with its high spatial resolution (~ 0.1 nm).[1] In this study, we investigated hopping motion of carbon monoxide (CO) on metal surface, which is one of the most simple and fundamental molecular motions at surfaces. Same as thermal diffusion, vibrations of the adsorbates are important because some vibrations couple with surface motions strongly. For example, a study using STM has revealed that internal stretching vibration of CO on Pd(110) (~ 250 meV) plays an important role.[2] We can control the energy of innelasticaly tunneled electrons from the tip of STM precisely, and those electrons can excite the vibration of aimed molecule. And recently, time resolved SFG study on Pt(553) has revealed that hindered rotation mode of CO (~ 51 meV) also contributes to hopping motion.[3] They performed the experiment at 100 K where hindered translation mode (~ 4 meV) is thermally excited enough. We took notice of this temperature effect. We performed the experiments at 4.8 ~ 45 K using STM (LT-STM, Omicron GmbH) equipped in an ultrahigh-vacuum chamber (< 3×10^{-9} Pa). The Cu(110) surface was cleaned by cycles of Ar ion sputtering and annealing cycles, and exposed to CO molecules below 50 K. First, by Inelastic Electron Tunneling Spectroscopy (STM-IETS) on CO/Cu(110) obtained at 4.8 K, the vibrational peaks of two surface parallel vibrations (hindered translation and hindered rotation) are clearly observed. Then, I tried Action spectroscopy on single CO molecule at various temperatures. In that spectra, the sudden change of the yields of hopping motion which corresponds to the internal stretching vibration of CO was observed. It means that anharmonic coupling between vibrations enables hopping motion of CO on Cu(110) surface easily. And temperature dependence of the yields of hopping motion does not obey the simple Arrhenius law. In the presentation, I will discuss the coupling between vibrations and molecular motions from these results.

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SS-TuP7 Effects of Interadsorbate Interactions on Surface Resistivity: Oxygen on Sulfur-Predosed Epitaxial Cu(100), ***C. Liu***, *R.G. Tobin*, Tufts University

Measurements of surface resistivity for oxygen absorbed on sulfur-predosed epitaxial Cu(100) reveal the existence and properties of two types of interadsorbate interactions between sulfur and oxygen: S-O repulsion and scattering suppression. The repulsive interaction causes oxygen atoms to first occupy adsorption sites far from the sulfur atoms. As a result the low-coverage variation of surface resistivity with oxygen coverage is unaffected by predosed sulfur, showing the linear dependence previously observed for oxygen on clean Cu(100).[1] As the oxygen coverage increases, oxygen begins to occupy sites near the sulfur atoms. At these sites the resistivity effect of the oxygen atoms is strongly suppressed, so that the sample resistance levels off, remaining unchanged even as oxygen continues to adsorb on the surface. With increasing sulfur precoverage both the maximum resistivity change and the oxygen coverage at which the leveling occurs decrease, because the number of sites unaffected by sulfur is reduced. Both the S-O repulsion and the scattering suppression have an effective range on the order of about 1.4 lattice spacings, with a rather sharp boundary. Both interactions presumably arise from a through-metal coupling involving the metal's local density of states.

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SS-TuP8 Wettability and Chemical Bonding of Water and Hydroxyl at Metal Surfaces, ***T. Schiros***, Stanford Synchrotron Radiation Laboratory, *O. Takahashi*, Hiroshima University, Japan, *K. Andersson*, DTU/Center for Individual Nanoparticle Functions, Denmark, *H. Öström*, Stockholm University, Sweden, *S. Yamamoto*, *L.-Å Näslund*, Stanford Synchrotron Radiation Laboratory, *L.G.M. Pettersson*, Stockholm University, Sweden, *A. Nilsson*, *H. Ogasawara*, Stanford Synchrotron Radiation Laboratory

The nature of the chemical bonding and structure of water and water co-adsorbed with hydroxyl at metal surfaces is of immense relevance to a number of important reactions in heterogeneous catalysis, including the water gas shift reaction over Cu and the fuel cell reaction over Pt and related alloys. We have combined core level x-ray spectroscopy, in both UHV and near-ambient conditions, with density functional theory to derive a detailed picture and comparison of the interaction of water and water plus hydroxyl with different metal surfaces, including Cu(110), Cu(111) and Pt(111). We demonstrate that the ability to form water-metal bonds, or wettability, is controlled by the degree of Pauli repulsion, which is influenced by both the electronic and geometric structure of substrates. At near ambient conditions, formation of OH groups by pre-adsorbed oxygen significantly modifies the ability to form water-metal bonds and plays a decisive role in the wetting of metal surfaces.

SS-TuP9 Low Temperature Microcalorimetry to Measure the Heat of Adsorption of Cyclohexene, Cis and Trans 2-Butene on Pt(111), *O. Lytken*, ***W. Lew***, *J.W. Harris*, *E.K. Vestergaard*, *C.T. Campbell*, University of Washington

The hydrogenation and dehydrogenation of cyclic hydrocarbons and short chain alkenes on platinum catalysts are important petrochemical reactions. We have used low temperature microcalorimetry measurements to determine their enthalpy of adsorption and sticking probability on Pt(111) at 100 K. Cyclohexene adsorbs intact at surface temperatures below 180 K, but decomposes at higher temperatures via several intermediates, including benzene and hydrogen starting at ~300 K. Trans-butene adsorbs intact below 200 K and cis butane adsorbs intact below 230 K. The difference between the heat of adsorption energy of the two isomers is compared with results from Zaera et al.[1] Since cyclohexene and butene both adsorb irreversibly on platinum, the traditional method to measure adsorption enthalpies, Temperature Programmed Desorption (TPD), cannot be used. Low temperature microcalorimetry makes it possible to measure the heats of formation of important reaction intermediates that are frequently unstable at room temperature. One of the major challenges of conducting low temperature calorimetric studies for small heats of adsorption is getting the microcalorimeter to detect small temperature changes on the order of 10 milliKelvins with minimal noise. This study explores modifications to the microcalorimetry apparatus to detect small adsorption energies.

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SS-TuP10 Electron Correlation Effects in Co Nano-Islands on a Nitrogen Covered Cu(001) Surface, ***Y. Takagi***, RIKEN, SPring-8 Center, Japan, *K. Nakatsuji*, *Y. Yoshimoto*, *D. Sekiba*, University of Tokyo, Japan, *Y. Harada*, RIKEN, SPring-8 Center, Japan, *K. Amemiya*, University of Tokyo, Japan, *Y. Takata*, RIKEN, SPring-8 Center, Japan, *T. Ohta*, University of Tokyo, Japan, *S. Shin*, RIKEN, SPring-8 Center and University of Tokyo, Japan, *F. Komori*, University of Tokyo, Japan

Recently, the atomic and electronic structures of magnetic nano-structure on surfaces have been intensively studied. We have investigated the initial growth of Co nano-islands on a nitrogen saturated Cu(001) c(2x2)-N surface by scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy and found that the nitrogen segregates on top of the Co islands and form Co-c(2x2)N structure.[1] In the present study, we discuss the electronic structure of this system in terms of electron correlation effect investigated by x-ray absorption spectroscopy (XAS) at both Co 2p and N 1s absorption edges comparing with the growth process studied by STM. N 1s XAS spectrum shows gradual increase of the absorption intensity just above the Fermi level with the increase of Co coverage. This indicates that the bonding of N 2p with Cu 3d changed into that with Co 3d which has smaller number of d electrons than Cu. The result strongly supports the segregation of N atoms. In the Co 2p XAS spectrum, a shoulder-like structure was found at 3 eV higher energy side of the main peak both at L_3 and L_2 absorption edges. Its relative intensity of this "3 eV satellite" to the main peak gradually decreases with Co coverage below 2 ML on average. In the case of Ni thin film, the origin of 3 eV and 6 eV satellites in the Ni 2p XAS spectrum are attributed to the configuration interaction of correlated electrons (CI) and multiple scattering in absorption process (MS), respectively.[2] We simulated XAS spectrum including the MS effect by FEFF code with the optimized atomic structure parameters obtained from first-principles calculation. However, the experimental results were not reproduced. Therefore, the origin of 3 eV satellites in our case is considered to be CI, indicating the presence of d^7 configuration as well as d^8. Comparing with the STM observation, the satellite is attributed to the mono-atomic height isolated Co-N islands. In such small islands, the charge transfer between Co and N would be different from that in the larger islands possibly by lattice compression.

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SS-TuP11 LEED and XPS Investigations of Surface Alloying of Ir on Cu(110), *P.F. Lyman*, ***S.S. Parihar***, University of Wisconsin-Milwaukee

Subsurface alloying is an interesting phenomenon that has been observed for several transition metals deposited on noble-metal surfaces, even where there is no bulk solubility of the two metals. In particular, while the bulk phase diagram of Ir-Cu has a large miscibility gap, subsurface alloying has been observed for Ir/Cu(100).[1,2] The Ir atoms appear to occupy ordered subsurface sites, forming a (2x1) reconstruction, with the required atomic place exchange taking place even for deposition at 200 K.[1] In the second layer, Ir and Cu atoms form Ir-Ir and Cu-Cu chains along every other close-packed direction. We evaporated submonolayer to monolayer Ir films on clean Cu(110) surfaces, and investigated the Ir-induced reconstruction using low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). The (1x1) LEED pattern changes into a (2x1) pattern for Ir coverages of close to half a monolayer. We expect that the Ir will still be confined to the near-surface region by the lack of bulk solubility, and we hypothesize that the Ir atoms will occupy subsurface sites based on their behavior on Cu(100). Based on LEED and XPS results, we propose that Cu and Ir form Ir-Cu-Ir-Cu chains along the close-packed direction for Ir/Cu(110)-(2x1), in contrast to the finding for Ir/Cu(100)-(2x1).

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SS-TuP12 Surface Diffusion of Hydrogen Atoms on Cu(111) Studied by Optical Diffraction from Hydrogen Density Patterns formed on Removable Templates of Xenon Monolayers*, Y.Y. Fei*, *X.D. Zhu*, University of California at Davis

We formed grating-like patterns of hydrogen adatom density on Cu(111) by using complementary patterns of xenon adatom density as the template. The template was pre-formed by laser-induced thermal desorption of a Xe monolayer on Cu(111) using the interference pattern of two coherent laser pulses. By following the evolution of hydrogen density gratings on Cu(111) from 153 to 183 K with linear optical diffraction, we found that the diffusion of hydrogen atoms on Cu(111) in this temperature range is the classical over-barrier hopping characterized by an activation energy barrier E_{diff} = 6.4 kcal/mol (or 279 meV) and a pre-exponential factor $D_0 = 2.0 \times 10^{-3}$ cm^2/sec. Based on the potential model proposed by Basdescu and coworkers for hydrogen on Ni(111), the WKB tunneling coefficient between the first vibrational excited states of a hydrogen adatom on Cu(111) is expected to be at least one order of magnitude smaller than that on Ni(111), indicating that the classical over-barrier hopping of hydrogen atoms could directly cross-over to under-barrier tunneling between ground-states on Cu(111).

SS-TuP13 Surface Temperature Dependence of Methane Dissociation on Ni*, V.L. Campbell*, *A.L. Utz*, Tufts University

The past decade has seen major groundbreaking work in the understanding of the role vibrational energy plays in the dissociation of methane on nickel surfaces. Yet, little work has been done on developing an understanding of the effect of surface temperature on this reaction. Two questions remain regarding the energy contained in the surface: First, how does the thermal bath of the surface atoms couple to the reaction coordinate? Second, does dislocation of the surface atoms alter the distribution of barriers to dissociation? Recent theoretical work suggests that the system is able to access lower barriers when the surface atoms are displaced above the plane of the surface. A change in the location of the Ni surface atom below the incident methane molecule could result in a lower energetic barrier making the reaction much more probable. As the surface temperature is increased, the probability of the incident methane molecule impacting on a displaced Ni atom increases. Experimentally, the biggest hurdle in understanding the dynamics that surface temperature plays in reactivity is deconvolting the gas-phase dynamics from the surface temperature dynamics. In thermal bulb experiments, it is not possible to discern the role of energy in the gas-phase comparatively to that of energy of the surface. Supersonic molecular beam experiments allow independent control of both the surface temperature, the impact energy and the average vibrational energy of the incident gas-phase molecules. Additionally, we use a narrow-bandwidth IR laser to prepare a non-equilibrium distribution of vibrational states, which allows us to determine the reactivity of select rovibrational eigenstates of the methane molecules over a range of incident kinetic energies and surface temperatures. The overall goal of these experiments is to determine the coupling of the vibrationally excited methane molecules to the phonon bath of the surface atoms and see what impact different surface temperatures have on reactivity.

SS-TuP14 Vibrational Effects on Precursor Mediated Surface Reactions*, D.F. Del Sesto*, *C.R. Thomas, N. Chen, A.L. Utz*, Tufts University

At high translational energies, methane dissociation on metal surfaces is generally shown to be dominated by a direct mechanism. The majority of methane molecules in a steam-reforming reactor have little translational energy, but are vibrationally excited. The vibrational energy content of these molecules is significant relative to the barrier to dissociation. In contrast, low translational energy molecules in conventional beam surface experiments are predominantly in the vibrational ground state. We propose experiments to explore the possibility that a precursor mechanism involving vibrationally excited molecules may be an important contributor to methane activation on metal surfaces at the high temperatures characteristic of industrial steam reforming reactors.

SS-TuP15 XPS Study of the Early-stage Oxidation Behavior of (Pt, Ni)$_3$Al(111) Surfaces in Air*, F. Qin*, Iowa State University and Ames Laboratory, *J.W. Anderegg, C.J. Jenks,* Ames Laboratory, *B. Glesson,* Iowa State University, *D.J. Sordelet,* Ames Laboratory, *P.A. Thiel*, Iowa State University and Ames Laboratory

We have studied the early stage of oxide formation on (111) oriented (Pt, Ni)$_3$Al single crystals in air. From X-ray photoelectron spectroscopy (XPS), the predominant surface oxide changed from NiO to Al_2O_3, as oxidation temperature increased from 900 to 1300 K. Some $NiAl_2O_4$(spinel) also formed at the higher temperatures. Under conditions where NiO and/or $NiAl_2O_4$ was present, it resided atop a layer of aluminum oxide, mixed in some cases with metallic Ni. By comparing samples that contained 0, 10 and 20 at. % Pt in the bulk, we found that the effects of Pt were to (1) promote the preferential formation of aluminum oxide over nickel oxide(s) in the top layer at all temperatures studied, (2) suppress the amount of metallic Ni mixed with Al_2O_3 in the underlying oxide region, (3) reduce the total oxide layer thickness, and (4) sharpen the interface between the oxide and the metallic alloy. The effects of Pt probably arise from a combination of sources: The non-oxidizing nature of Pt relative to Ni or Al; the substitution of Pt for Ni that occurs in the Ni_3Al lattice structure; and the increase in Al activity that is induced by Pt.

SS-TuP16 Ion Beam-Induced Formation and Interrogation of Metal Nanoclusters*, J.A. Yarmoff*, *A.B. Arjad, P. Karmakar, G.F. Liu,* University of California, Riverside, *Z. Sroubek*, Czech Academy of Sciences

Metal nanoclusters are important systems that display quantum size effects and have remarkable catalytic activity. We utilize low energy (0.5-5 keV) ion beams as a simple, but efficient means for both the controlled production and the characterization of nanoclusters. Low energy Ar$^+$ beams enable control of the size and shape of nanoclusters because of the curvature dependence of ion sputtering. The neutralization of scattered low energy alkali ions provides a sensitive measure of the localized electronic states. It was previously shown that scattered alkalis couple to atomic-like states specific to Au nanoclusters grown by deposition, and the neutralization probability is a function of the cluster size.[1] We further showed that sputtering a thin Au film on TiO_2(110) with Ar$^+$ forms self-organized nanoclusters that display quantum size effects.[2] The scattered alkali neutral fractions increase as the cluster dimensions decrease, indicative of the quantum size effects, and the data shows that the electronic structure of clusters grown by deposition and by sputtering are similar. In this work, Li$^+$, Na$^+$ and K$^+$ ions are employed to probe metal nanoclusters formed by both deposition and sputtering, and the dependence of neutralization on cluster size is compared. Au or Ag is first deposited on an insulating or semiconducting substrate, and self-organized clusters are produced either during the deposition, or by Ar$^+$ sputtering a thin film. The ion scattering NF's have different dependences with respect to cluster size for each alkali projectile. The microscopic mechanisms responsible for the formation of the nanoclusters, and for the charge exchange between scattered alkali ions and the nanoclusters, will be discussed.

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SS-TuP17 The Formation of Iron Oxide Nanoparticles and Thin Films on Au(111)*, N.A. Khan*, *C. Matranga*, National Energy Technology Laboratory (NETL)

Iron-based catalysts, including iron oxides, are an important class of materials with relevance to Fischer-Tropsch catalysis and gas-sensing applications. The controlled growth of nanoparticles and atomically thin films on single crystal surfaces allows for systematic studies of how size, shape, and atomic structure affect the chemical reactivity of these materials. We have studied the formation of monolayer thick iron oxide nanoparticles and thin films on the reconstructed Au(111) surface. STM, XPS, ISS, and LEED were used to evaluate the structure and composition of the iron oxide nanoparticles and films as a function of growth conditions. Iron oxide growth was achieved by first depositing iron nanoparticles on Au(111) at room temperature. At coverages of 0.2-0.5 monolayer (ML), Fe forms triangular islands at the elbows of the Au(111) herringbone reconstruction. At higher coverages, the particles begin to coalesce and the second and third layers of Fe start to form before the first layer is complete. The oxidation of Fe was performed by exposing the nanoparticles to molecular oxygen at 323 K and 423 K, followed by annealing to 500-700 K. XPS results indicate that the Fe is oxidized, with a shift of the Fe 2p peak to a higher binding energy. Atomically-resolved STM images show the formation of iron oxide particles that are hexagonal in shape and one monolayer high with a diameter of 10-20 nm. STM images at higher iron oxide coverages also show evidence of a non-coincidence overlayer lattice with a short periodicity of 0.25-0.3 nm modulated by a larger periodicity of approximately 3.5 nm. The larger periodicity results from a moiré pattern formed between the iron oxide overlayer and the underlying Au(111) surface.

SS-TuP18 Binding Character for a Xe Adatom on Nb (110), ***C.Y. Fong***, *M.C. Qian, X.D. Zhu,* University of California at Davis, *L.H. Yang*, Lawrence Livermore National Laboratory, *S. Dag*, Oak Ridge National Laboratory

We determined the binding characteristics of a Xe adatom on Nb (110) using density functional theory within the local density approximation. The on-top site is the most favorable for adsorption with a binding energy of 271 meV. Although the preference for the on-top site is the same as on the (111) surface of Pt and a number of other fcc metals, there is a discernable charge accumulation showing a weak covalency between Xe and its nearest-neighboring Nb atom. Compared to the Xe on Pt case, the differences are manifested by (i) the hybridization of Xe p-state with nearly half-filled Nb d-states causes the energy levels of Xe p-states to shift downward by 1.2 eV with the p_z-state splitting off from the p_x- and p_y-states, and (ii) the shifted Xe p-states have relatively narrow bandwidths due to the off-resonant condition between the p-states of an isolated Xe and the Nb d-states. They can be attributed to the less than half filled d shell of the Nb atom inducing stronger hybridization with the p-states of the Xe atom. †Work done at Lawrence Livermore National Laboratory under the auspices of the US Department of Energy under Contract No. W-7405-Eng-48.

SS-TuP19 Coverage and Temperature Dependence of LEED Streak Intensity on Li adsorbed on Cu(001) Surface at Lower Coverage, ***H.M. Mitani***, Fukuoka University of Education, Japan

Arced shape streaks, which connect four fold spots are observed in LEED experiment, in Li adsorbed system on Cu (001) surface, where the four fold spots correspond to c(2x2) structure of adsorbed Li atoms. The streaks originate from second neighbor pair (d=2a) of Li atoms in the c(2x2) structure sites. Especially, there are two types of adatoms in terms (y-)component of wave number of the streak ($k_y = \pi /a$). Both types of the sub-lattices give an anti-phase relation on the streak. If Li atoms are fully occupied on the c(2x2) sites at a coverage 0.5, the intensity is vanished. While, if the coverage is less than 0.5, a deviation of the number of atoms in the two types of sub-lattices gives a certain intensity of the streak; it becomes strongest at coverage 0.25 (H.Mitani et al. J.Phys.Soc.Jpn. 2005). In this paper, using Monte Carlo simulation, we obtain arrangements of Li atoms on adsorption sites on Cu (001) surface, as a lattice gas model, in a range of coverage (0-0.5), and a certain temperature width. By Fourier transforming of the arrangement of the atoms, we obtain almost square type streaks, which correspond to the arced shape steaks in the experiment. The reason of change from the line streaks in the square to the arced one, as shown in the experiment has already been clarified (H.Mitani et al. J.Phys. Cond.Matt. 2006). It is not a matter in the present paper. We also obtain coverage and temperature dependence of an intensity of the streak and also the four fold spots. Especially the coverage dependence of the intensity, reproduces a result of experiment; it increase along the coverage (0-0.25), and decrease in coverage (0.25-0.5). We also obtain the coverage-dependence of the intensity of the four fold spots. In terms of temperature-dependence, there is no result in experiment now. We obtain that the intensity of the streaks, broadly speaking, increases as temperature. Especially at coverage 0.5, it shows as Shottkey type behavior. On the other hand, the intensity of the four fold spots, shows second order transition, which has a certain phase transition point.

SS-TuP20 Thickness Dependence of the Interaction of NO_2 with Thin MgO(100) Films Grown on Ag(100) as Studied Photoemission Spectroscopy, *D.E. Starr, Ch.D. Weiss,* Lawrence Berkeley National Laboratory, *S. Yamamoto, A. Nilsson,* Stanford Synchrotron Radiation Laboratory, *M. Salmeron,* ***H. Bluhm***, Lawrence Berkeley National Laboratory

The adsorption of NOx compounds onto alkaline-earth metal-oxide surfaces has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NOx storage compounds for controlling emissions during combustion under fuel lean conditions. In this work we have studied the adsorption of NO2 onto MgO(100) thin films grown on Ag(100) ranging from 2 ML to over 8 ML in thickness and NO2 exposures from a few hundred Langmuir up to twenty thousand Langmuir at 300 K. We have used the Ambient Pressure Photoemission Spectroscopy experiment at beamline 11.0.2 of the Advanced Light Source to characterize this system using both core level and valence band photoemission as well as Auger-yield Near Edge X-ray Adsorption Spectroscopy. On thin films (~ 2 ML thick) we observe exclusively the adsorption of NO2 with coverages of ~ 0.5 ML for all exposures. As the film thickness increases the initial amount of NO2 adsorbed onto the surface decreases (~0.05 ML on films with thicknesses greater than ~5 ML) and we observe the formation of NO3 with increasing exposures. The final amount of NO3 on the surface of films thicker than 5 ML is ~ 0.3 ML. This indicates that the adsorption and reaction of NO2 on the surfaces of MgO(100) can, to some extent, be controlled by growing MgO(100) films of specific thicknesses. The mechanism of NO2 stabilization on the surfaces of thin MgO(100) films on Ag(100) will also be presented.

SS-TuP21 Comparative Study of the Electronic Structure of ZrB_2 and ZrB_{12}, ***L. Huerta***, *R. Escamilla, E. Regalado,* Universidad Nacional Autónoma de México, *M. Flores*, Universidad de Guadalajara, México

X-ray photoemission spectroscopy (XPS) and Ultraviolet photoemission spectroscopy (UPS) are used to compare the electronic structures of ZrB_2 and ZrB_{12}. The Zr 3d and B 1s core levels associated with the chemical states of ZrB_2 and ZrB_{12} were identified, the Zr 3d core level shows a spin-orbit split $3d_{5/2}$ and $3d_{3/2}$ while that the B 1s core levels exhibit a single asymmetric peak typical of a metallic boride. Comparing with Zr metallic, boron and ZrO_2 reference materials, for ZrB_2 we observed a positive chemical shift for B 1s and a negative chemical shift for Zr $3d_{3/2}$ while that in ZrB_{12} the chemical shift in B 1s and Zr $3d_{3/2}$ is inverse, suggesting that a some charge transfer occurred from the Zr atoms to the B atoms in the ZrB_2 and from the B atoms to the Zr atoms in ZrB_{12}. The measured valence bands using UPS and XPS are consistent with band-structure calculations indicating a higher density of states (DOS) at E_F for ZrB_{12} compared to ZrB_2. That's suggesting that the T_c in ZrB_{12} is due to B 2p and Zr 4d-derived DOS at E_F.

SS-TuP22 Reactivity of Model Iron and Iron Oxide Surfaces and Nanoparticles with Chlorinated Hydrocarbons, ***G.S. Parkinson***, *Z. Dohnalek, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Iron and iron oxide surfaces and nanoparticles have been shown to be catalytically active in the destruction of chlorinated hydrocarbons in environmental remediation applications. We employ a combination of molecular beam and surface analytical techniques to synthesize and characterize model iron and iron oxide thin films grown on Pt(111) and supported nanoparticles deposited on FeO(111)/Pt(111). The chemical activity of these model catalysts is explored using temperature programmed desorption and X-ray photoelectron spectroscopy. The reactivity of a series of chlorinated methanes is explored both anhydrously and in the presence of coadsorbed water. The experimental methods, results, and their mechanistic implications will be presented.

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-TuP23 High Temperature Scanning Tunneling Microscopy on the Ion Conducting Material YSZ(111), *A.J. Carter, J. Lahiri,* ***M. Batzill***, University of South Florida

Most STM studies are performed on samples with good electron conductivity. Here we demonstrate STM measurements on the ion conductor yttrium stabilized zirconia (YSZ) at elevated temperatures. YSZ is the prototypical solid electrolyte that finds applications as an ion conductor for solid fuel cells and in gas sensing applications. In spite of these important technological applications the fundamental surface properties of ZrO2 are not well investigated. The wide band gap (>5eV) of zirconia and its poor electron conductivity hamper surface studies. Here we show that at elevated temperatures of about 600 K the ion conductivity is high enough to enable scanning tunneling microscopy investigations of this material and thus open the door for the investigation of the surface and defect structure at the atomic scale.

SS-TuP24 Nature of Photoactive Species on the TiO_2 Nanotube Thin Films, *T.-L. Hsiung, Y.Y. Hsu,* ***H.P. Wang***, National Cheng Kung University, Taiwan

The TiO_2 nanotube thin films were synthesized using ZnO nanorods as a template on the silica substances. By scanning electron microscopy (SEM), the TiO_2 nanotube thin films having a pore opening of about 200 nm were observed. Experimentally, the TiO_2 nanotube thin films have a very high activity in photocatalytic degradation of 2-chlorophenl (2CP) (220 mg/gTiO_2 hr) under UV/Uis irradiation. By pre-edge X-ray absorption near edge spectroscopy (XANES), the photoactive species may be distinguished in three titanium structures such as A_1 (TiO_4), A_2 ((TiO_4)=O), and A_3 (TiO_6). Interestingly, the A_2 species with a Ti=O and four Ti-O bonds to form a polyhedron in the TiO_2 nanotube thin films might be the main active sites involved in the photocatalytic degradation of 2CP. The TiO_2 nanotube thin films were also used in photocatalytic degradation of toxic pollutants such spill oils in the harbor or seashores.

SS-TuP25 Reaction Properties of NO over the Rh/Al_2O_3/NiAl(110) Model Catalyst, ***I. Nakamura***, *A. Takahashi, T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency of noble metal is an important subject. In this study, we investigated the NO reaction properties using Rh supported model catalyst. The model catalyst was prepared by deposition of Rh onto the Al_2O_3 thin film. It was shown that the NO dissociation activity on Rh deposited on Al_2O_3 is higher than that on Rh(111). Furthermore, we found that the NO dissociation activity on the Rh supported model catalyst increased by annealing treatment, where the activity increased with increasing heating temperature up to 500 K, and then decreased above 600 K. These results indicate that the atomic efficiency of Rh for NO dissociation is enhanced by supporting on Al_2O_3. To clarify the effect of Al_2O_3 support on Rh, we examined the NO adsorption state on the Rh supported model catalyst using IRAS. The IRA peak due to NO adsorbed on hollow site was observed at 1615 cm^{-1} for the surface without heating, which agreed with the frequency observed for Rh(111). In contrast, the peak due to NO adsorbed on bridge site was newly observed at 1645 cm^{-1} for the surface annealed to 500 K. Thus, we considered that the Rh surface structure changes from (111) face to (100) face by heating to 500 K. We previously found that the NO dissociation activity on Ir(100) was about twice of that on Ir(111), which was consistent with the relationship between the Rh supported model catalyst annealed to 500 K and Rh(111). Therefore, the enhancement of atomic efficiency of Rh is due to a change of the Rh surface structure to (100) face with a high NO dissociation ability. We concluded that the effect of Al_2O_3 support on NO dissociation is not electronic effect on Rh, but stabilization of (100) Rh surface structure.

SS-TuP26 Quantum-Resolved Photodesorption and Photodissociation Studies of Organic Nitrates and Halides on Ice, ***B. Olanrewaju***, *T.M. Orlando*, Georgia Institute of Technology

Several mechanisms have been proposed for the release of reactive species from organic halides and nitrates on ice during tropospheric ozone depletion episodes at polar sunrise. However, the description of the initial reactions that lead to the formation of precursors for these species remains incomplete because the surface enhanced catalytic effect of ice/snow interfaces is not well understood. Since the photochemical processing of interfaces involving these systems may be an important source of reactive species; we have carried out state resolved studies of photochemical production and release of Br and NO_x from selected organic halides and nitrates adsorbed on ice. Specifically, we utilized resonance enhanced multiphoton ionization to detect the 300 nm photoproduced and desorbed NO and Br (Br^*) from photoexcitation of bromoform and isopropyl nitrate adsorbed on crystalline and amorphous ice. We report cross sections and discuss the potential atmospheric relevance.

SS-TuP27 Antirelaxation Surface Coatings for High-Density Alkali-Metal Magnetometers, ***D.M. Rampulla***, *S.J. Seltzer, M. Romalis, S.L. Bernasek*, Princeton University

Atomic magnetometers containing spin-polarized alkali-metal atoms are capable of detecting magnetic fields with a sensitivity superior to that found in SQUIDs; however, a current issue with atomic magnetometers are depolarizing collisions between alkali-metal atoms and the cell walls. An inert buffer gas can be used to slow diffusion of spin-polarized alkali-metal atoms to cell walls, but a preferable solution would be a high-quality antirelaxation surface coating that would diminish the depolarization events that lead to the loss of spin-coherence and reduce the need for buffer gas. Although some coatings have been proven effective, paraffin and others presently in use typically can not operate at the relatively high temperatures ($T > 100$°C) for cesium and ($T > 150$°C) for potassium required for high-density magnetometers; therefore, it is desirable to find an effective antirelaxation coating suitable for these temperatures. In previous work, we have found that a coating of octadecyltrichlorosilane (OTS) at $T > 150$°C can allow a potassium atom to collide more than 2000 times with the walls of a spherical borosilicate glass cell before depolarizing. However, spherical glass cells are not easily studied with surface science techniques (X-ray photoelectron spectroscopy and reflection-absorption infrared spectroscopy), thus we constructed a reusable alkali vapor cell for measuring antirelaxation properties of multiple flat surfaces coated with various monolayers (chlorosilanes and phosphonic acids). In addition to antirelaxation properties, the coatings were tested for reactivity toward alkali metals and temperature stability.

SS-TuP28 Co-deposited $BaTiO_3$ Nanocomposites in Polymer and LiF Host for Embedded Capacitor Applications, ***A. Biswas***, *I.S. Bayer, P.C. Karulkar*, University of Alaska, Fairbanks

Embedding capacitors has become a critical system need for high performance miniaturized electronic systems. Fabrication and performance constraints make developing materials, processes, structures, and devices for embedded capacitor technology a great challenge. Nanocomposites comprising metal or ceramic nanoparticles in polymer have recently emerged as promising candidates. They offer potential for attaining high capacitance value, high frequency performance, process compatibility, and reliability, while being lightweight, volume-efficient, flexible and low-cost. Among other materials, barium titanate is considered one of the most promising dielectric materials due to its high dielectric constant to blend with polymers to develop high-value capacitors. However, the existing techniques that are mostly based on chemical synthesis and high temperature (>1000°C) sintering followed by blending with the polymers. This makes implementation difficult. In this paper, we present a single-step method based on electron-beam assisted vapor-phase codeposition in vacuum that allows ambient temperature fabrication of nanocomposites (~0.5 μm thick) comprising ferroelectric barium titanate nanoparticles in polymer (polymethyl methacrylate and polyurethane/polyaniline block copolymer) as well as inorganic matrices (LiF). Ferroelectric properties of barium titanate can be achieved without post deposition annealing. Preliminary capacitance-frequency results exhibit flat capacitance densities around 12-15 nF/cm^2 in most of the devices with a low tangent loss (~ 0.03) and leakage current of about 70 nA/cm^2 in the -20 V to +20 V bias region over a frequency region of 10-100 MHz. Exposing the capacitors to prolonged heating at 125°C for several days to investigate the effects of thermal stress on the device capacitance resulted in a slight reduction in the capacitance density which may be due to the possible transition from ferroelectric to paraelectric phase in barium titanate. However, overall high-frequency response improved significantly due to minimized ferroelectric loss that resulted in self-resonance frequencies occurring beyond 250 MHz. The paper will describe the novel application of vacuum codeposition technique, very encouraging physical and electrical characterization results, and their potential for embedded technology.[1]

[1] Financial support of the Defense Microelectronics Activity is acknowledged.

SS-TuP29 Heats of Adsorption and Growth Mode of Lithium on MgO(100), ***N. Ruzycki***, *J. Farmer, J.H. Baricuatro, C.T. Campbell*, University of Washington

MgO(100) is a very well studied model oxide surface in model oxide-supported metal catalysis. Lithium-promoted MgO is an active catalyst for the partial oxidation of methane. Inherent surface defects change the surface reactivity and act as anchors for catalytically active metal nanoparticles. This study explored the adsorption energetics and growth mode of lithium atoms on stochiometric and defected MgO(100) surfaces, in a unique UHV chamber designed for sensitive adsorption calorimetry measurements, electron and ion spectroscopies and LEED. The MgO(100) thin films (4 nm thick) were grown on a Mo(100) single crystal. The lithium was vapor deposited onto the MgO(100) film under UHV conditions using a pulsed metal atom source. The sticking probability of lithium was near unity. The heat of adsorption for lithium on MgO(100) was 260 kJ/mol initially, dropping with coverage to reach the heat of sublimation of pure lithium metal (159 kJ/mol) above 0.5 ML. Low energy He+ ion scattering (LEIS) revealed the growth mode for Li adsorption: Li initially wets the surface as adatoms up to ~0.5 ML, after which 3D islands of Li grow. Work function measurements yielded a change with coverage typical for alkali metal adsorption on late transition metals, with a 2.2 eV initial decrease associated with cationic Li adatoms, followed by an increase back to the value for bulk Li metal as the Li depolarizes at higher coverages due to dipole-dipole repulsions in the Li adlayer. Argon ion beam damage created defects which adsorb Li more strongly than MgO(100) terraces (up to 370 kJ/mol or more).

SS-TuP30 Strong Interaction between BaO and Al_2O_3 in NO_x Storage Materials: Correlation between Model and High Surface Area Catalysts, ***C.-W. Yi***, *J.H. Kwak, C.H.F. Peden, C.M. Wang, J. Szanyi*, Pacific Northwest National Laboratory

A series of Ba-containing NO_x storage reduction (NSR) model catalysts were prepared by reactive layer-assisted deposition (RLAD) of Ba onto Al_2O_3/NiAl(110) and investigated with surface science techniques. Upon NO_2 exposure the model catalysts demonstrated corresponding properties to the high surface area ones. Initially nitrite species form, and then Ba ions are pulled out from the surface at higher NO_2 exposures, resulting in the formation of ionic barium nitrates. The formation and agglomeration of $Ba(NO_3)_2$ clusters were observed by infrared reflection absorption (IRA) and x-ray photoelectron spectroscopies (XPS) for the model systems, and by Fourier transform infrared (FT-IR), time-resolved synchrotron x-ray diffraction (TR-XRD), and high resolution scanning transmission electron microscopy (HR-STEM) for the high surface area catalysts. The correlation between the model and real catalysts shown here for NO_2 adsorption and reaction strongly emphasizes the value of well-designed surface science studies aimed at understanding practical catalytic systems, and this approach ultimately can allow us to develop NSR catalysts with better performances.

SS-TuP31 Substitution of Carbon for Oxygen in TiO_2 for Photocatalysis Applications*, **P. Nachimuthu**, S. Andrews, V. Shutthanandan, M.H. Engelhard,* Pacific Northwest National Laboratory*, T. Tyliszczak, D.K. Shuh,* Lawrence Berkeley National Laboratory*, S. Thevuthasan, M.A. Henderson*, Pacific Northwest National Laboratory

In semiconductor photochemistry, the redox potential of a photocatalyst is strongly modified by its band gap, which in turn dictates the energy separation of the electron-hole (e^-/h^+) pairs. The position of the bands relative to the band gap with respect to the electron donor and acceptor orbitals in the reactants determines the degree of overlap between adsorbate molecular orbitals and the electronic states associated with the e^-/h^+ pairs. TiO_2 is one of a few candidate materials with promising photocatalytic properties although the optical absorption spectrum of pure TiO_2 has poor overlap with the solar spectrum and high e^-/h^+ pair recombination rates. However, anion doping of TiO_2 is known to red-shift its optical absorption spectrum into the visible region and as a result, visible light phtotoactivity has been observed for N-doped TiO_2. Recently, we have investigated C-doped $TiO_2(110)$ rutile using ion beam implantation as a function of temperature and dopant concentrations. Subsequent 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), near-edge x-ray absorption fine structure (NEXAFS), Rutherford backscattering spectrometry (RBS) (both random and channeling), and nuclear reaction analysis (NRA). NRA measurements along the channeling and random geometries clearly indicate the substitution of carbon for oxygen in the TiO_2 lattice under certain conditions. XPS data on sputter cleaned samples show the presence of carbon in two different environments with binding energies of 282.4 eV (carbide; Ti-C interaction) and 284 eV (C-C and/or C-O interactions). However, sputter cleaning followed by annealing in oxygen, eliminates the higher binding energy features suggesting that sputtering effects play a role in modifying the carbon environment in the rutile lattice. Carbon K-edge NEXAFS data are consistent with the XPS findings. Both XPS and NEXAFS show that non-carbidic interactions were significantly developed following annealing at high temperatures, although no evidence of carbon release was found from these C-doped samples.

SS-TuP32 Formation and Surface Chemistry of TiO_2 Nanoparticles on Au(111)*, **Y.Z. Le**, N. Stojilovic, R.M. Osgood,* Columbia University*, J. Hrbek*, Brookhaven National Laboratory

Titania (TiO_2) nanoparticles are formed on Au(111) surfaces under ultrahigh vacuum conditions using the method of reactive-layer-assisted deposition (RLAD). In this method, physical-vapor deposited Ti on H_2O/Au(111) reacts with oxygen from water to produce TiO_2 nanoparticles. During heating of the substrate unreacted water molecules and its fragments desorb leaving the TiO_2 nanoparticles on Au(111) surfaces. Characterization of the nanoparticles is performed using Auger electron spectroscopy (AES) whereas temperature programmed desorption (TPD) experiments are used to probe the surface chemistry of water and halogenated alkanes on these nanoparticles. Effect of titania coverage and particle size on subsequent desorption kinetics and surface chemistry is investigated. In particular, we have probed the reactive formation of these particles as a function of surface annealing temperature and observed changes in desorbed species. This formation chemistry is aided by a separate scanning tunneling microscopy (STM) study of the particle morphology, which reveals nanoparticles of 1-5 nm in size.

SS-TuP33 Characterization of Ceria-Titania Nanostructures: Insights into the Catalytic Performance*, **A.S. Karaoti**, S.V.N.T. Kuchibhatla, T. Spalding, K. Suresh babu, S. Seal*, University of Central Florida

Oxide based semiconductors such as ceria and titania are used prolifically for a host of catalytic applications. Recently there has been an upsurge in the research, marrying the two materials for enhanced catalytic applications. A marked increase in the catalytic performance of the mixed ceria-titania oxides have been reported by various groups. However, a clear understanding of the underlying mechanisms is still at large. The present work focuses on the characterization of ceria mixed titania using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC) and Photoluminescence (PL) experiments. The retention of more catalytic anatase phase at higher temperature upon mixing with ceria and the electronic properties which result in enhancing the catalytic behavior are critically analyzed. Influence of increasing ceria concentration on phase stability, particle size and electronic properties of titania will also be discussed.

SS-TuP34 Surface Structure of $BaTiO_3$ (001)*, **D.B. Li**, R. Shao, A. Kolpak, A. Rappe, D.A. Bonnell*, University of Pennsylvania

Although oxide surfaces have been extensively studied over the last 2 decades, the atomic structure of $BaTiO_3$ (001) has received relatively little attention as a consequence of a variety of experimental challenges. The fundamental aspects of reactions on ferroelectric surfaces are critical to a range of device applications and $BaTiO_3$ (001) is the prototypical model surface. On overcoming these challenges we have used STM, nc-AFM, LEED and AES, to show that this surface adopts a family of reconstructions depending on thermo-chemical history. Most of these structures have not been observed previously. Some of the reconstructions are reminiscent of those that occur on $SrTiO_3$ (001) but the details differ significantly. Using a combination of density functional theory and ab initio thermodynamics, we compute the surface phase diagrams with oxygen potential as a dependent variable, since this is a critical variable in the experiment. The stabilities of reconstructions with Ba-adatoms, O-vacancies and Ti-O clusters are compared for different thermo-chemical conditions. Comparisons of the results of the calculations with the STM and nc-AFM results are used to construct atomic models for the reconstructed surfaces.

SS-TuP35 Water Dissociation on $TiO_2(110)$ Supported Au Catalyst: A DFT Study*, **G. Wang**, J. Jiao*, Nankai University, China

The present DFT calculations have clearly reproduced the experimental phenomena for H2O dissociation on TiO2(110) supported Au catalyst (including both Au cluster and scattered Au-atoms). Our results indicate that the Au-atom scattered on TiO2 strongly interacted with the supported TiO2, and compared with the supported metallic Au particle, is the most active site for the H2O dissociation reaction to occur due to the low activation energy (0.80eV). Second, the neighboring supported metallic Au particles have no effect on the catalysis activity of scattered Au-atoms for adsorbed H2O dissociation; Third, the supporting TiO2(110) has positive effect as regard to the scattered Au-atom-catalyzed H2O dissociation reaction, because it could reduce the reaction activation energy by about 0.37eV; on contrast, it has little effect on the activity of metallic Au particles; Fourth, the calculations also indicated that the active site for molecular decomposition reaction is just opposite to that of its reverse reaction, that is, as the reverse reaction of H2O dissociation, H(a)+OH(a)=H2O(a), has a less activation energy on supported metallic Au particles than on scattered Au-atoms.

SS-TuP36 Preparation and Chemical Modification of Nanoparticle Layers by Plasma Treatments*, B. Gehl,* University Bremen, Germany*, A. Frömsdorf, V. Aleksandrovic,* University Hamburg, Germany*, T. Schmidt, J. Falta,* University Bremen, Germany*, H. Weller,* University Hamburg, Germany*, **M. Baeumer***, University Bremen, Germany

Nanoparticles deposited as thin films on oxidic substrates represent a highly interesting class of materials systems not only for physical (e.g. magnetic) but also chemical applications, such as heterogeneous catalysis for example. A flexible and relatively simple way to prepare such layers is to wet-chemically synthesize nanoparticles in colloidal solution and deposit them onto a flat substrate by spincoating or a comparable method. In most cases the as-prepared particles are surrounded by a shell of organic molecules stabilizing the colloidal suspended state. To freely access the properties of the metallic particle surface for measurement or application, it is necessary to remove this shell of physically obstructing and chemically passivating ligands. It is important that the method used to strip the particles of their organic sheath neither disturbs the particle material, the substrate nor the structure of the layer. This can be achieved by exposing the deposited nanoparticles to a mild plasma removing the ligand shell through a combination of sputtering and etching processes with free radicals. It will be demonstrated that both reducing and oxidizing plasmas can be used for this purpose. Moreover, by varying plasma gasses and parameters, it is also possible to modify the chemical state of the particles selectively but leaving the lateral arrangement on the surface undisturbed. The contribution will shed light on the possibilities and limits of the approach also comparing the results to experiments where the ligand shell was removed by thermal treatment. Another aspect that will be addressed is the risk of chemical interactions with the support material induced by the plasma treatment.

SS-TuP37 Behavior of Deuterated Ethanol on Zircaloy-4 Surfaces*, Y.C. Kang, **J.Y. Park***, Pukyong National University, S. Korea

The surface chemistry of deuterated ethanol on the zircaloy-4 surfaces was investigated by means of temperature programmed desorption(TPD) and Auger electron spectroscopy (AES) techinques. The cleanliness of the zircaloy-4 was checked by AES and the purity of deuterated ethanol was checked by quadruple mass spectrometer (QMS) after several cycles of freeze-pump-thaw method. Depending on the adsorption temperatue, water evolution was changed as peak maximum position and absolute peak intensity. Even highly pure deuterated ethanol was used, hydrogen exchange was observed in this experiment. As the amount of exposed deuterated ethanol increased, the oxidation state of zirconium was changed from metallic to zirconia form. During linear heating of the deuterated ethanol dosed zircaloy-4 surfaces, hydrogen evolution was observed. This implys that this system has potential of production of hydrogen.

SS-TuP38 Design and Construction of a Batch Microreactor for Investigations of Heterogeneous Catalysts Deposited on Flat Supports, ***M. Sushchikh**, J. Colby, L. Cameron, W. Tang, A. Kleiman-Shwarsctein, J.N. Park, H. Metiu, E. McFarland*, University of California, Santa Barbara

A five microliter volume batch microreactor system has been developed for the investigations of the reaction kinetics over low surface area catalysts deposited on flat supports including submonolayers of metals on single crystals. The main features of the reactor are: micro-probing capability using principle of variable leak valves (minimal altering of the amount of gases in the reactor volume); direct probing of the gases into ultra-high vacuum (UHV) mass-spectrometer volume (high sensitivity); enclosure of the reactor volume in larger tank (leak-proof by design). The reactor is made of UHV compatible components and is ready to be attached to an UHV chamber equipped with linear stage sample transfer. The reactor has been tested at initial total pressure 500 Torr, but both, lower and higher pressures are possible. The temperature is controlled over the range of 20°C to 250°C. The reactor allows monitoring of the reactions over time from tens of minutes to hours. The performance of the reactor has been demonstrated for CO oxidation reaction over Pd foil.

SS-TuP39 Growth and Physical Properties of Epitaxial Metastable $Hf_{1-x}Al_xN$ Alloys Deposited on MgO(001) by Ultrahigh Vacuum Reactive Magnetron Sputtering, ***B.M. Howe**, J. Bareño,* University of Illinois at Urbana-Champaign*, M. Stoehr,* Université de Haute Alsace, France*, M. Sardela, J.G. Wen, J.E. Greene,* University of Illinois at Urbana-Champaign*, L. Hultman,* Linköping University, Sweden*, A.A. Voevodin,* Air Force Research Laboratory*, I. Petrov*, University of Illinois at Urbana-Champaign

Epitaxial metastable $Hf_{1-x}Al_xN$ alloys with 0 = x = 0.50 were grown on MgO(001)substrates at 600°C by ultrahigh vacuum reactive magnetron sputtering from Hf and Al targets in 90 % Ar + 10 % N2 discharges at 7 mTorr. X-Ray diffraction and crosssectional transmission electron microscopy show that $Hf_{1-x}Al_xN$ alloys are single crystals with the B1-NaCl structure. Rutherford backscattering spectroscopy investigations reveal that all films are slightly overstochiometric with N/(Hf+Al) = 1.05 ± 0.05. The relaxed lattice parameter decreased linearly from 0.4519 nm with x = 0 to 0.4438 nm with x = 0.50, compared to 0.4320 nm expected from the linear Vegard's rule. We find a metastable single phase field that is remarkably broad given the large lattice mismatch (~ 9 %) between the two alloy components. Alloying HfN with AlN leads to an increase in hardness (~ 30% to 32.4 ± 0.7 GPa), as well as nanostructured compositional modulations due to the onset of spinodal decomposition.

SS-TuP40 Effect of Water Vapor on Monolayer Features Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces[1], ***K. Kimura**, S.C. Langford, J.T. Dickinson*, Washington State University

Low doses of energetic electrons can produce monolayer etch pits on alkali halide cleavage surfaces.[2] Similarly, UV laser radiation can roughen steps and produce monolayer islands and pits on NaCl at fluences well below the macroscopic damage threshold.[3] Step edges on NaCl are highly vulnerable to erosion due to high densities of kinks. In NaCl, step erosion is dramatically accelerated in the presence of 10^{-5} Pa water vapor.[4] In this work, we compare atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in vacuum. Since atmospheric water vapor affects all these surfaces, AFM was performed under dry nitrogen. Prior to laser exposure, the principal features are straight, monatomic cleavage steps. Fifty 248-nm pulses at 100 mJ/cm^2 are sufficient to produce monolayer islands and to roughen cleavage steps in ultrahigh vacuum on all three materials. Island-free zones are observed on both the upper and lower terraces along cleavage steps. The island densities and the width of the island free-zones vary significantly with laser fluence. Islands appear to be formed from material eroded from the steps. Similar laser exposures in the presence of 10^{-5} Pa water vapor produce monolayer etch pits, rather than islands, on KBr and KCl. Higher laser fluences are required to produce pits on NaCl. Calibrated quadrupole mass spectrometry on the products emitted during laser irradiation shows emission intensities consistent with that required to form the etch pits. In the presence of 10^{-5} Pa water vapor, the detected intensities are typically several times higher than in ultrahigh vacuum. Islands and etch pits are also observed on surfaces exposed to low doses of 2 keV electrons; again, these features are dramatically affected by the presence of water vapor. Although mechanism for the effect of water vapor is not clear, the dissociative adsorption of water at surface halogen vacancies is expected to play a role.

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Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-WeM

Catalysis for Hydrogen Storage and the Hydrogen Economy

Moderator: G. Fisher, Delphi

8:00am **EN+SS+TF-WeM1 Catalysts for Hydrogen Production by Sulfur-Iodine Thermochemical Water Splitting Cycle**, ***L.M. Petkovic***, *D.M. Ginosar, K.C. Burch, H.W. Rollins, S.N. Rashkeev, H.H. Farrell*, Idaho National Laboratory

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels and without generating gasses considered to be responsible for global warming. The sulfur-iodine (S-I) thermochemical cycle appears promising for producing hydrogen from water. The S-I cycle consists of three simultaneous reactions: the decomposition of hydroiodic acid (HI) to produce hydrogen and generate iodine for recycle, the decomposition of sulfuric acid to produce oxygen and generate sulfur dioxide for recycle, and a main reaction where incoming water and the recycle chemicals react to regenerate HI and sulfuric acid. Both HI and sulfuric acid decomposition reactions are facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions of the sulfuric acid decomposition reaction present a significantly challenging environment for catalytic materials. In this work a number of titania (rutile)-supported platinum-group metal (i.e., Pt, Ir, Pd, Ru, and Rh) catalysts were investigated for this reaction. To develop an understanding of the factors that cause catalyst deactivation, density-functional theory-based first-principles calculations and computer simulations for transition metal particles positioned on titania (rutile) were performed. In addition, experimental determination of the activity and stability of activated carbon catalysts for the HI decomposition reaction will also be presented. Results of activated carbon characterization analyses, including surface area, temperature programmed desorption, Boehm's titration results, and contact pH of the activated carbons will be discussed.

8:20am **EN+SS+TF-WeM2 Trends in Hydrogen Splitting on Transition Metals at 1 Bar**, ***M. Johansson***, *O. Lytken, I. Chorkendorff*, Technical University of Denmark

Despite the fact that the interaction of hydrogen with various metal surfaces has been studied extensively under ultra-high vacuum conditions, there is very little data available for the hydrogen dissociation rate on clean surfaces at pressures on the order of 1 bar. Here we investigate the hydrogen splitting rate for a number of transition metals by measuring the rate of the H-D exchange reaction. Experiments are also carried out in the presence of CO, in order to investigate the mechanism behind CO poisoning of the anode catalyst in proton-exchange membrane fuel cells. The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.[1] Model catalysts are prepared by electron-beam evaporation of metal spots onto a highly ordered pyrolytic graphite (HOPG) substrate. Typically, the spots are 1 mm in diameter and 50 Å thick. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The gas is sampled 0.2 mm from the center of the spot, and the sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D_2 in H_2, with or without the addition of 10 ppm CO. The temperature was varied in the range 40 - 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES) before and after exposure to gases in the high-pressure cell. In order to take the back-reaction (HD splitting) into account, a simple model for the H-D exchange reaction is used. It is assumed that the sticking probability, S, is the same for H_2, HD and D_2. Under the conditions of interest here, S is mainly dependent on the coverage of adsorbed species on the catalyst surface. Once S has been extracted from the experimental data, the dissociative adsorption/desorption rate for pure H_2 at 1 bar can be calculated. So far, the metals Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt have been investigated. The measured values for S are reasonably consistent with data obtained with high hydrogen coverage under vacuum conditions. Metals which bind hydrogen strongly are expected to give lower values for S. However, S is found not to correlate with the heat of adsorption for hydrogen as determined at low coverage under vacuum conditions. The most active metal for hydrogen splitting is Ru, closely followed by Rh. For these metals, S is close to being independent of temperature. Pt and Pd give comparable values for S in the temperature range investigated, but the temperature dependence is stronger for Pd than for Pt. The activity then decreases in the order Ir, Co and Ni. No measurable activity is found for Cu. The addition of 10 ppm CO lowers the splitting rate significantly on all the metals, also at 200 °C. Among the investigated metals, Pt and Ir are the ones most sensitive to CO poisoning.

[1] M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum., 75 (2004) 2082.

8:40am **EN+SS+TF-WeM3 Catalytic Autothermal Reforming of Renewable Fuels at Millisecond Times**, ***L. Schmidt***, University of Minnesota **INVITED**

We compare the reforming of different types of biofuels by autothermal reforming at millisecond contact times to produce synthesis gas, hydrogen, and chemicals. Fuels examined are alcohols, esters, carbohydrates, biodiesel, vegetable oil, and solid biomass. Biofuels generally have higher conversions than fossil fuels because the hydroxyl and ester linkages in these fuels produce higher sticking coefficients than for saturated alkanes. Consequently, conversions of all biofuels in these processes are nearly 100%. Highly oxygenated feedstocks tend to produce mostly syngas with little olefins or oxygenated products because surface reactions dominate, and these larger products are formed predominantly by homogeneous reaction processes after all oxygen is consumed. Recent results on production of syngas by reactive flash volatilization of nonvolatile liquids and solids will also be described. We show that, by impinging cold liquid drops or small solid particles onto the hot catalyst surface, the process can be operated in steady state with no carbon formation for many hours. This occurs because, while pyrolysis of vegetable oils and carbohydrates at low temperatures produces carbon, above ~600oC the equilibrium shifts to produce syngas rather than solid carbon.

9:20am **EN+SS+TF-WeM5 Transient Kinetic Analysis of Intermediates in Steam Reforming on Oxide Supported Cu Catalysts**, ***Y. Yang***, *R. Disselkamp*, Pacific Northwest National Laboratory, *C.T. Campbell*, University of Washington, *C. Mims*, University of Toronto, Canada, *D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

Formate hydrogenation was proposed to be the surface reaction channel forming methanol through reverse water gas shift by previous investigators [Chorkendorff et al., J. Vac. Sci. Technol. A, 10(4), 2277 (1992)]. The interconversion and decay of copper formates on a Cu/Gamma-Al2O3 catalyst are studied here using an apparatus that combines in-situ transmission-FTIR of adsorbed species and mass spectrometric detection of reactor effluent during transient kinetic analyses (transmission-FTIR/MS/TKA). At 573 K, ~ 2% CO and 0.07% methanol conversions were obtained by sending 2.5 bar H2:CO2 3:1 flow at 10 sccm through the reactor. It is also observed that at lower temperature, 353 K - 433 K, surface formate species are formed with the input feed stream as observed by IR. The kinetics of their transient reactivity (e.g., titration) are examined after switching to either a reducing (H2), oxidizing (2% N2O in He), or inert gas (He, Ar) feed stream. The kinetics of total formate decay at 306, 363, and 433 K under H2, He, or Ar gas exposure are observed to be comparable, suggesting that a thermal unimolecular desorption and not hydrogenation alone, is operative. However upon hydrogen exposure it is observed that within the broad formate IR band(s) there is internal species exchange which indicates two types of different formates are formed. Similar studies are presented for a SiO2 supported polycrystalline Cu sample to help identify the formate species. Methanol steam reforming on both samples were also studied for further understanding of the reverse reaction processes.

9:40am **EN+SS+TF-WeM6 Model Catalysts for Water-Gas Shift Reaction**, *S. Ma, X. Zhao, J.A. Rodriguez, P. Liu*, ***J. Hrbek***, Brookhaven National Laboratory

Gold supported on ceria was shown to be very active catalyst for water-gas shift reaction and low temperature CO oxidation. Both reactions are used to purify hydrogen by removing CO, a poison of fuel cell catalysts, and are therefore of importance in the hydrogen economy. In this presentation we will discribe the preparation, characterization and reactivity of an â?oinverseâ? model catalyst, i.e. CeOx nanoparticles supported on the Au(111) surface. Using STM and XPS we found that physical vapor deposition of Ce metal leads to formation of surface intermetallic compounds after annealing. The Ce-Au surface alloys have low reactivity toward oxygen, however, we were able to prepare CeOx by vapor-deposition of Ce in a moderate oxygen pressure (10-7 torr). Elongated flat ceria nanoparticles are 0.5 nm thick, several nanometers long and anchored mostly to steps. Atomically resolved images of the ceria island show well-ordered CeO2 (111) surfaces with few defects. Ce 3d photoelectron spectra were used to identify the oxidation state of Ce in oxides prepared by different methods. In general, oxidation at temperatures below 400 K leads to formation of poorly ordered nanoparticles of Ce2O3 and higher temperature annealing in background oxygen is needed to form CeO2. Individually, neither Au(111) nor CeO2(111) have any activity in the WGS reaction, while both the Au/CeO2(111) model catalyst and the CeOx/Au(111) inverse model catalyst show significant activity in high pressure experiments. Our photoemission data indicate that Ce2O3 nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO2 nanoparticles are inactive. As the water dissociation could be the rate limiting step in the WGS reaction, our ability to identify dissociation products under vacuum conditions and to link them with the structural characterization at the atomic level reinforces reaction models in which the oxide support is not a simple spectator and plays an essential role in the WGS process. Acknowledgement: This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

10:40am **EN+SS+TF-WeM9 Double Role of Water in Fuel Cell Oxygen Reduction Reaction**, ***H. Ogasawara***, *L.-Å Näslund, J.B. MacNaughton, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

A management of appropriate humidity level is necessary for the fuel cell to operate. The oxygen reduction reaction (ORR) occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. Using XPS and XAS, we have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

11:20am **EN+SS+TF-WeM11 Adsorption and Dehydrogenation of Carborane on Pt(111)**, ***A. Tillekaratne***, *M. Trenary*, University of Illinois at Chicago

The techniques of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to explore the dehydrogenation on a Pt(111) surface of 1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{12}$, also known simply as carborane. Complex hydrides, such as the boranes and carboranes, are of interest as possible hydrogen storage materials because of their high hydrogen content. Many hydrides are quite stable and catalysts are needed to promote the release of hydrogen at low temperatures. The carbon and boron atoms of the $C_2B_{10}H_{12}$ carboranes occupy the vertices of a slightly distorted icosahedron and have a hydrogen weight percentage of 8.3. There are three isomers of these icosahedral carboranes, of which the ortho form (the 1,2 isomer) is the most readily available. The icosahedral structure of the boron-carbon cage structure of carborane is also adopted by the boron-rich solid boron carbide. The similarity in the structures of carborane and boron carbide has led to the successful use of carborane as a precursor gas for the growth of boron carbide thin films. However, the detailed mechanism by which carborane dehydrogenates to form boron carbide has not been previously investigated. At submonolayer coverages at 85 K the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm^{-1}, and a weak C-H stretch at 3090 cm^{-1} that indicate molecular adsorption at low temperature. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm^{-1}. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, which is also indicative of the formation of partially hydrogenated surface intermediates. Further analysis of the data may permit definitive identification of the surface intermediates formed during the course of carborane dehydrogenation on the Pt(111) surface.

11:40am **EN+SS+TF-WeM12 Short Range Order of Ti Dopants in Al(111): Implications for Hydrogen Storage**, ***E.M. Muller***, Brookhaven National Laboratory, *C.V. Ciobanu*, Colorado School of Mines, *P. Zahl, P. Sutter*, Brookhaven National Laboratory

Complex metal hydrides can potentially satisfy the need for lightweight, high-capacity hydrogen storage materials, a key requirement for the Hydrogen Economy. However, for most known complex hydrides the solid-state reactions involved in hydrogen release are not reversible, and their rates are low under moderate ambient conditions. The discovery that small amounts of Ti make the decomposition of sodium alanate ($NaAlH_4$) to NaH and Al reversible at moderate temperatures and pressures[1] has demonstrated doping with catalysts as a promising route to induce reversible hydrogen storage and fast reaction kinetics. A fundamental understanding of the catalytic effect of Ti in $NaAlH_4$ could form the basis for rational strategies to optimize a broader class of complex hydride hydrogen storage materials. We combine experiments on single crystal model surfaces and density-functional theory (DFT) to establish the role of near-surface Ti in the re-hydrogenation of NaH and Al to $NaAlH_4$. A likely primary effect of Ti is the formation of catalytically active surface sites enabling the facile dissociative chemisorption of H_2 on Al, which itself has very low affinity to H_2. Using chemically specific scanning tunneling microscopy and DFT we identify the stable configurations of Ti atoms incorporated into Al(111) surfaces as a first step to identifying potential catalytically active sites. Surprisingly, despite a higher surface energy of Ti (i.e., a driving force for diffusion into sub-surface sites), our observations show a pronounced stabilization of Ti at the Al surface where its catalytic effects are maximized. STM shows a large population of a specific Ti-atom pair complex, which has been predicted to catalyze H_2 dissociation.[2] We discuss the origin of this pairing, and the interaction of atomic and molecular hydrogen interactions with these surface Ti complexes.

[1] B. Bogdanovic and M. Schwickardi. J. Alloys Comp. 253-254, 1 (1997).

[2] E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu and P. Sutter., Appl. Phys. Lett. 90, 151917 (2007).

12:00pm **EN+SS+TF-WeM13 Alane Formation on Al(111) and Ti-doped Al(111)**, ***S.C. Chaudhuri***, Washington State University, *J.-F. Veyan, S.C. Schaäfer*, Rutgers, The State University of New Jersey, *J.T. Muckerman*, Brookhaven National Laboratory, *Y.J. Chabal*, Rutgers, The State University of New Jersey

Complex metal hydrides, such as $NaAlH_4$, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in $NaAlH_4$, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na_3AlH_6 to the hydrogen-rich $NaAlH_4$, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H_2 dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. We have combined in-situ infrared absorption spectroscopy with first principles calculations to investigate the reaction of atomic hydrogen reacts with Al surfaces. As previously observed,[1] IR spectra show that alanes are formed upon H exposure. Alanes are highly mobile species at or near room temperature and desorb from Al(111) surfaces at higher temperatures mainly as AlH, AlH_3 and Al_2H_6.[2] Using FT-IR we show that the size of the alanes formed on Al(111) depend on the temperature of the sample. For low temperatures (Ã90K), small alanes such as AlH_3 and Al_2H_6 are predominant. At higher temperatures (Ã250K), bigger alanes are formed. When the Al(111) surfaces are doped with 5% Ti, the Ti containing sites are reactive, dissociating molecular hydrogen, and thus act as a pump to generate hydride species on Al surfaces that subsequently convert into alanes. LEED is used to test the validity of first principles c alculations predicting that Ti atoms occupy hollow sites on the Al(111) surface. Using TPD, the nature of desorbed species from Al(111) and Ti-doped Al(111) surfaces have been analyzed as a function of the sample temperature after either atomic H or H_2 exposures. This presentation summarizes hydrogen dissociation on Ti/Al(111), and alane formation and mobility on both Al(111) and Ti/Al(111) surfaces.

[1] Eden P. Go, Konrad Thuermer, Janice E. Reutt-Robey, Surf. Sci. 437 (1999) 377

[2] Hara, M.; Domen, K.; Onishi, T.; Nozoye, H., J. Phys. Chem., 95, (1), (1991) 6-7

Surface Science

Room: 608 - Session SS1-WeM

Oxide Surface Reactivity

Moderator: V.M. Bermudez, Naval Research Laboratory

8:00am **SS1-WeM1 Influence of Ferroelectric Polarization on Adsorption on $BaTiO_3$**, *D.B. Li*, ***M. He***, *J. Garra, D.A. Bonnell, J.M. Vohs*, University of Pennsylvania

Many perovskite oxides such as $BaTiO_3$ undergo a phase transition from a ferroelectric tetragonal phase to a paraelectric cubic phase at readily accessible temperatures. In the ferroelectric state the material is polar and has a bulk electric dipole whose orientation can be controlled via application of an external electric field. While it has been suggested that the orientation of the ferroelectric dipole on the surface may affect adsorption and reaction of species from the gas phase, examples demonstrating the ferroelectric control of surface reactivity have to date been elusive. In this talk we will present what we believe are the first definitive examples of the influence of ferroelectric polarization on the surface reactivity of BaTiO$_3$. In the first example, demonstrates the effect of ferroelectric polarization on the adsorption of CO$_2$ on oxygen vacancies on the surface of a BaTiO$_3$(001) single crystal. Sub-micron sized out-of-plane domains with the polarization oriented perpendicularly inward (c$^-$) or outward (c$^+$) from the surface were produced on the BaTiO3(001) sample using an AFM tip. Frequency modulation, scanning surface potential microscopy (FM-SSPM) was then employed to measure the potential change of the ferroelectric domains before and after exposure of the poled surface to CO$_2$. It was observed that CO$_2$ caused a larger decrease in the surface potential for c$^-$ domains relative to the c$^+$ domains, indicating a difference in the amount of CO$_2$ adsorbing on each domain. In the second example, the amount of methanol that adsorbed on an oriented, BaTiO$_3$ thin film supported on TiO$_2$(110) under UHV conditions was found to be dependent on the orientation of the ferroelectric dipole. In this case the sample was poled by heating above Tc and then placing it in contact with an electrode to which a small + or - voltage was applied. For a constant exposure, the amount of CH$_3$OH that adsorbed at 300 K was found to increase in the following order c$^-$ > unpoled > c$^+$. This result has been attributed to a polarization dependent interaction of weakly bound CH$_3$OH molecules prior to dissociative adsorption at defect sites.

8:20am **SS1-WeM2 Effect of Poling Direction on the Reactivity of Ferroelectric Oxide Surfaces**, *Y. Yun, M. Li,* Yale University*, L. Kampschulte,* Ludwig Maximilians Universität, Germany*, D. Liao, B. Lukanov, **E.I. Altman***, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or strongly adsorbing polar molecules. Because opposite charges must be screened on opposite surfaces, different reactivities are expected on positively and negatively poled surfaces. We have studied the surface atomic composition, structure and reactivity of LiNbO$_3$(0001) surfaces. The surfaces appeared nearly indistinguishable in spectroscopic and diffraction measurements: both surfaces were (1x1) and appeared almost fully oxygen terminated in low energy ion scattering spectra. Despite the structural similarities, differences in reactivity between positively and negatively poled surfaces were observed using TPD. Polar molecules including 2-propanol and acetic acid adsorbed much more strongly on the positive surfaces as evidenced by desorption peak temperatures over 100 K higher. Further, the TPD curves were found to depend unusually strongly on the heating rate. This efect could be attributed to the change in polarization with temperature - the pyroelectric effect- creating a temperature-dependent heat of adsorption. Including this effect, an 11 kJ/mole higher 2-propanol heat of adsorption was estimated for the positive surface. These results will be compared with adsorption of non-polar molecules where the polarization changing with temperature is not expected to affect the strength of the adsorbate-surface interaction. The results for LiNbO$_3$ will also be compared with PbZr$_x$Ti$_{1-x}$O$_3$ thin films to determine the generality of the observed phenomena.

8:40am **SS1-WeM3 The Interaction of NO$_2$ with MgO(100) Studied with Photoemission Spectroscopy**, ***D.E. Starr**, Ch.D. Weiss,* Lawrence Berkeley National Laboratory*, S. Yamamoto, A. Nilsson,* Stanford Synchrotron Radiation Laboratory*, M. Salmeron, H. Bluhm*, Lawrence Berkeley National Laboratory

NOx compounds are very harmful environmental contaminants commonly formed in combustion processes. Their adsorption onto the surfaces of alkaline-earth metal-oxides has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NOx storage compounds for controlling emissions during combustion under fuel-lean conditions. In this work we have studied the adsorption of NO2 on MgO(100) films grown on Ag(100) using photoemission spectroscopy. Many of the previous experimental studies of this system were performed at low temperatures with subsequent thermal heating under Ultra-High Vacuum conditions. In this study we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption and reaction of NO2 onto MgO(100) at 300 K and 10-6 torr NO2 pressures for exposures ranging from a few Langmuir up to twenty thousand Langmuir. At these conditions, we find that the NO2 initially adsorbs as NO2 with low coverage (~0.05 ML). Upon increasing exposure, we observe a reduction in the coverage of NO2 and the presence of adsorbed NO3. Further, at high exposure we find increasing coverage of NO3 (~0.30 ML) without the presence of NO2 on the surface. This indicates that the production of NO3 on the surface likely occurs via initial NO2 dissociation which produces adsorbed O which then oxidizes NO2 to form NO3.

9:00am **SS1-WeM4 The Interaction of NO$_2$ with BaO: From Cooperative Adsorption to Ba(NO$_3$)$_2$ Formation**, ***J. Szanyi**, C.-W. Yi, J.H. Kwak*, Pacific Northwest National Laboratory

The adsorption and reaction of NO2 on a thick (> 30 ML), pure BaO film deposited onto an Al2O3/NiAl(110) substrate at 90 K and the higher temperatures were investigated with surface science techniques such as temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS) techniques. For the first time, it was clearly demonstrated that BaO readily reacts with NO2 to initially form nitrite-nitrate ion pairs by the cooperative adsorption mechanism predicted by theoretical calculation. These nitrite/nitrate pairs readily form even at 90 K. In the decomposition process of these pairs first the nitrite species release an NO molecule, and nitrate species decompose in two steps: at lower temperature as NO2 only, then, at higher temperature, as NO + O2. The results of NO2 adsorption/reaction on this model system are identical to those we have found on a high surface area 20 wt.% BaO/Î³-Al2O3 sample with the exception of surface nitrates that were only observed on the high surface area material.

9:20am **SS1-WeM5 Reactivity of Low-dimensional Oxide Nanostructures**[*], ***F.P. Netzer***, Karl-Franzens University Graz, Austria **INVITED**

Oxide materials in nanostructured layers exhibit physical and chemical properties that are significantly different from their respective properties in macroscopic bulk phases. This novel behaviour forms the basis for many potential applications of oxide nanostructures in diverse areas of the emerging nanotechnologies. Here we discuss the physico-chemical properties of ultrathin oxide overlayers (nanolayers = thickness ≤ 10 ML), grown on metal single crystal surfaces, in terms of their novel structural concepts, their modified electronic behaviour and their sensitivity to changes in the chemical environment. A multitude of experimental techniques (STM, SPA-LEED, XPS, NEXAFS, UPS, HREELS) in conjunction with ab initio DFT model calculations has been applied to characterise the oxide nanolayers deposited on Pd and Rh substrate surfaces. The oxide materials considered comprise nickel, manganese and cobalt oxide phases. Specifically, we will discuss chemical and structural aspects of phase transformations of Mn-oxide overlayers in the 1-10 ML range on Pd(100). Emphasis will be put on the structural transition from the MnO(100) to the MnO(111) orientation as a function of the chemical potential of oxygen and on the oxidation of MnO to Mn$_3$O$_4$ surface phases. The chemical interaction of NiO(100) surfaces, epitaxially grown on Pd(100), with metallic cobalt and Co-oxide overlayers is addressed from the viewpoint of generating sharp antiferromagnetic-(anti)ferromagnetic interfaces. It is shown that CoO(100) can be grown epitaxially on NiO(100) and that a 1-2 ML CoO buffer layer can inhibit the oxidation reaction of Co metal overlayers, thus forming a sharp AFM-FM interface. The oxidation of metallic quasi-one-dimensional (1-D) Ni nanowires, formed on the stepped Rh(15 15 13) surface, to 1-D Ni-oxide phases is illustrated. The latter are compared to the 2-D Ni-oxide phases that develop by reactive physical vapour deposition on the same stepped Rh surface, in order to assess the dimensionality aspects in the formation of oxide nanostructures.

[*] Supported by the Austrian Science Funds (FWF) and the EU STREP programme GSOMEN.

10:40am **SS1-WeM9 Adsorption Energetics of Ag on CeO$_2$(111)**, ***J.H. Baricuatro**, J. Farmer, C.T. Campbell*, University of Washington

The energetics of Ag deposition on well-defined films of CeO$_2$(111) were investigated using adsorption microcalorimetry. Thin films of CeO$_2$(111) were grown on Pt(111) at 700 °C by thermal evaporation of Ce under a reactive atmosphere of O$_2$. Ag was evaporated from an effusive vapor source and the resultant surface structures were probed using a combination of low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and low-energy He$^+$ ion scattering spectroscopy (LEIS). The adsorption of Ag exhibited a sticking coefficient that is close to unity (0.98), independent of coverage. The enthalpy of adsorption of Ag was initially low (ca. 200 kJ/mol) but increased with Ag coverage up to the sublimation enthalpy of bulk Ag. The effect of surface oxygen vacancies on the adsorption energy of Ag was also investigated.

11:00am **SS1-WeM10 Redox Properties of HCOOH over CeO$_2$ Surfaces: Pathways to Surface Oxidation and Reduction**, ***S.D. Senanayake**, D.R. Mullins*, Oak Ridge National Laboratory

This study undertakes a close scrutiny of the reaction of HCOOH, the simplest C-1 carboxylic acid, with the surfaces of CeO$_2$, a well defined (111) oriented lanthanide oxide system. HCOOH is an important precursor to the formation of CO$_2$ and H$_2$ in the water-gas-shift (WGS) reaction, in which ceria (in combination with nobel metal particles) is also used as a stable support rich in oxygen storage capacity. The HCOOH is observed to adsorb by way of a formate intermediate species (HCOO$^-$) through the dissociation of the acidic H over both CeO$_2$ (Ce^{+4}) and CeO$_x$ (Ce^{+4}/Ce^{+3})

surfaces. This species will be compared to other C1 adsorbates observed such as methanol[1] and formaldehyde[2] reacting over ceria, which yield methoxy (CH_3O) and dioxymethelene (CH_2O_2) species, respectively. The dissociated H species recombines with surface O and desorbs as H_2O <300K. At 300K polarization dependent C K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) data suggest that the formate is adsorbed in a bi-dentate structure with the O-C-O plane oriented normal to the surface. In addition to water, Temperature Programmed Desorption (TPD) spectra indicate the evolution of CO_2 (m/z 44) and H_2 (m/z 2) around 350-400K followed by only CO desorption in two regimes at 450 and 525K. The net result is a slight reduction of the ceria substrate. In a reversal of roles, formic acid oxidizes the reduced CeO_x surface. No H_2O or CO_2 desorbs at lower temperatures but is replaced with desorption of only CO and H_2 between 450-600K. Soft X-ray Photoelectron Spectroscopy (sXPS) indicates that formate is again the only surface intermediate. With the introduction of Rh nanoparticles to the reduced and oxidized Ceria surfaces the formate decomposition is observed over ceria. Furthermore, sXPS also shows CO adsorption on Rh (C1s ~286eV) that decomposes further to give Rh-C species (284.5eV) which can be compared to CO reaction over Rh / CeO_x surfaces.[3]

[1] J. Phys. Chem. B., 110 (32) 15994 (2006).

[2] Surf. Sci., 600 1540 (2006).

[3] J. Catal., 188 340 (1999).

[*] Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

11:20am **SS1-WeM11 Hydrogen Diffusion on $TiO_2(110)$ at Elevated Temperatures**, ***S.-C. Li***, *J.M. White,* University of Texas at Austin, *Z. Zhang, B.D. Kay, Z. Dohnálek*, Pacific Northwest National Laboratory

The TiO_2 chemistry has been widely investigated in both fundamental science and technical applications, due to its intriguing chemical properties. One of the important applications is the photochemical hydrogen production from H_2O. On a prototypical $TiO_2(110)$ surface, the bridge-bonded oxygen (BBO) vacancies have been shown to be the primary reactive sites for H_2O dissociation yielding geminate pairs of OH groups. In this study we use variable temperature Scanning Tunneling Microscopy (STM) to investigate intrinsic hydrogen diffusion along the BBO rows as a function of temperature. The hopping rates deduced from the consecutively collected STM images at temperatures ranging from 320K to 420K are analyzed. The prefactors and activation barriers are extracted as a function of OH-OH separation using the Arrhenius analysis. A comparison of the hopping rates for hydrogen and deuterium shows a strong isotope effect.

The research described in this presentation 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.

11:40am **SS1-WeM12 The Adsorption of Cysteine and Co-Adsorption of Cysteine and Gold on $TiO_2(110)$**, *E. Ataman, C. Isvoranu, J.N. Andersen,* ***J. Schnadt***, Lund University, Sweden

The bonding of organic molecules to transition metal oxide surfaces such as TiO_2 is a concern central to the construction and optimization of molecule-based devices. Organic–inorganic interfaces are presently receiving increasing attention due to both fundamental and application interests. Interest also derives from the role of TiO_2 as a support for metal catalyst particles such as Au nanoclusters, which act as an excellent catalyst for, e.g., the low temperature CO oxidation reaction. The cluster size of the Au particles has to remain within an optimum range for the catalyst to preserve its activity. However, the Au clusters are prone to coalescence as a function of temperature and gas exposure. In order to retain the catalytic activity it is important to hinder this growth process. The idea developed here is to use L-cysteine as a spacer between the clusters, since it strongly binds to the TiO_2 surface via its carboxylic group. It is well-known that the thiol group of cysteine interacts with gold, which then might establish the missing link between the gold clusters and the spacer molecules. We have investigated the adsorption of L-cysteine as well as the co-adsorption of L-cysteine and gold on rutile $TiO_2(110)$ by means of x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and scanning tunneling microscopy (STM). The spectroscopy results clearly show that the notion of a molecule-TiO_2 substrate bond via the carboxylic group of the molecule is correct. This finding receives further support from the STM measurements. The basic geometry characterized by the oxide-carboxylate bond is retained even for the co-deposition case; however, the S 2p spectra indicate an additional interaction between the gold clusters and molecules. An interesting additional feature of the spectroscopy experiments was the observation of very rapid beam damage, which we attribute to a facile change in the protonation status of the amino and thiol functional groups.

12:00pm **SS1-WeM13 Density Functional Theory Study of Hydrogen Cyanide and Formamide over Rutile TiO_2 (110) and (011) Surfaces**, ***P.R. McGill***, *H. Idriss*, The University of Auckland, New Zealand

Formamide is a compound of considerable interest, owing to its ability to yield nucleobases during photoreaction over TiO_2 in both aqueous[1] and ultrahigh vacuum conditions.[2] The mechanisms for this synthesis have been postulated to involve the generation and subsequent decomposition of HCN polymers on the surface. While a number of experimental studies have investigated formamide and HCN adsorption to the surfaces of TiO_2,[2,3,4] computational work has focused on their interaction with metal surfaces.[5] In this study, a series of periodic DFT calculations are conducted on formamide and HCN adsorption to the (110) and (011) bulk terminated surfaces of rutile TiO_2, employing plane wave basis sets and the PBE exchange correlation functional. Dissociative adsorption appears favoured for formamide on both investigated surfaces; the formamide molecule binding in a bridging manner across two surface Ti sites analogous to that of formic acid on the rutile TiO_2 (110) surface. Molecular adsorption through the carbonyl oxygen's interaction with the surface Ti is also found to be energetically favourable, though to a lesser extent. No stable interaction mode is observed for molecular adsorption through the N atom to the surface Ti species, in agreement with IR studies[3] conducted on formamide over polycrystalline TiO_2. HCN was found to strongly preference toward molecular adsorption in an orientation perpendicular to the surface, with the nitrogen binding to a surface Ti. Dissociative adsorption is found to be less favourable than molecular adsorption, with dissociative adsorption through the C atom yielding a greater stability than through the N atom. Adsorption modes parallel to the surface (which are reported on metal surfaces[5]) do not appear to represent energy minima, and convert back to perpendicular configurations on geometry optimisation.

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Surface Science

Room: 611 - Session SS2+EM+TF-WeM

SAMs and Organic Films I

Moderator: H. Fairbrother, Johns Hopkins University

8:00am **SS2+EM+TF-WeM1 Scanning Tunneling Microscopy Growth Study of a Columnar Liquid Crystalline Hexaazatriphenylene Derivative on Au(111)**, ***S.D. Ha***, Princeton University, *Q. Zhang, S. Barlow, S.R. Marder,* Georgia Institute of Technology, *A. Kahn*, Princeton University

The growth of a discotic liquid crystal derivative of tris(thieno)hexaazatriphenylene (THAP) is studied with scanning tunneling microscopy (STM). An electron transport material with relatively high electron affinity (4.59eV), THAP is expected to form columnar stacks in a thick bulk film. It is shown with STM that on Au(111), the first four monolayers of THAP molecules order in such columnar mesophases. The first monolayer forms a square 10.1Å x 10.1Å unit cell with one molecule per cell. However, this is much smaller than expected, and it may be due to buckling caused by the substrate interaction or in-plane molecule-molecule interaction. The second monolayer, at partial coverage, grows commensurate to the first monolayer in a rectangular herringbone with two molecules per 15.7Å x 14.0Å unit cell. The molecules tilt in order to conform to the packing of the first layer and the interlayer interaction controls the molecular orientation. Yet upon full coverage of the second monolayer, the intralayer interaction prevails and the molecules reorganize into a hexagonal close-packed (HCP) structure without obvious tilt. The unit cell is rhomboidal with dimensions 21.0Å x 22.2Å and one molecule per cell. Moreover, the rotational orientation of the molecules forms a herringbone pattern, with alternating rows of the HCP structure switching between two opposite orientations. As for the third and fourth monolayers, STM images indicate that they have HCP geometry with the same dimensions as the second layer. Given the tendency of molecules similar to THAP to stack into columns, it is likely that because the third and fourth layers have the same in-plane structure as the second layer, they are commensurate to the latter. Thus, on Au(111), THAP readily grows in the expected columnar liquid crystal fashion directly from the interface layer, and the columns are hexagonal close-packed with negligible molecular tilt.

8:20am **SS2+EM+TF-WeM2 UHV-STM Studies of DNA Bases on Au(111)**, ***W. Xu***, *R. Otero, M. Schock*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark, *R. Kelly, L. Kantorovich*, King's College London, UK, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

The self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has recently attracted much attention as on one hand, such studies provide invaluable insight into fundamental interactions between these molecules. On the other hand, NA base molecules and DNA molecules are particularly interesting as promising building blocks for the bottom-up fabrication of functional supramolecular nanostructures on surfaces within the emerging area of nanotechnology. From a biological point of view, the self-assembly processes in DNA and RNA molecules are controlled by i) cross-strand interactions between NA base molecules, which are dominated by hydrogen bonds (H-bonds), ii) stacking interactions between NA base molecules along the strand, and iii) the interactions of NA base molecules with water molecules and metal ions, such as Na+, K+. Among these interactions, the hydrogen bonding between NA base molecules plays a crucial role in determining the conformation and biochemical properties of DNA and RNA molecules. Hence, it is important and interesting to study the fundamental interactions between NA base molecules at the single molecule level to reveal the exact physicochemical nature of the biological systems. Here we will show our recent experimental progress on four individual NA base molecules (guanine, adenine, cytosine, thymine) that are adsorbed on Au(111) surface under Ultrahigh Vacuum (UHV) conditions. We demonstrate by variable-temperature scanning tunnelling microscopy (VT-STM) experiments that guanine and adenine form 2D island with well-ordered structures through hydrogen bonds, and the so-called guanine quartet structure is found to be stabilized by the cooperative hydrogen bonds. Interestingly, cytosine only forms disordered 1D filamentary structure by fast cooling the sample, whose behavior could be described as a 2D organic glass. Thymine in the first stage (low surface coverage) also forms 1D filamentary structure steered by hydrogen bonds. However, when the surface coverage is increased, the filaments could merge into 2D well-ordered islands by van der Waals (vdW) interactions. Moreover, we have also investigated that the thymine 2D island can be broken back into the 1D hydrogen bonded filaments by STM manipulation, which further confirm that we are able to directly probe the hierarchy of bond-strengths involved in the surface self-assembly of multifunctional organic molecules with highly anisotropic interactions.

8:40am **SS2+EM+TF-WeM3 Understanding Molecular Exchange on Surfaces: Controlling and Elucidating the Mechanism of 1-Adamantathiolate Monolayer Displacement**, ***H.M. Saavedra***, *T.J. Mullen, C.M. Barbu*, The Pennsylvania State University, *A.A. Dameron*, University of Colorado, *V.H. Crespi, P.S. Weiss*, The Pennsylvania State University

We have investigated the solution-phase displacement kinetics of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and electrochemical desorption. The displacement reaction can be described by the fast insertion of n-dodecanethiolate at defects in the original 1-adamantanethiolate monolayer, which nucleates island growth and is followed by eventual slow ordering of the n-dodecanethiolate domains. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to describe this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained over a hundred-fold variation in n-dodecanethiol concentration. Analysis on a model-free basis suggests that displacement is a scale-free process within this concentration regime. The crucial role of the adsorbate lattice, along with the thermodynamic driving forces, rationalizes the rapid and complete displacement of 1-adamantanethiolate monolayers and explains why other monolayers reach kinetic traps that result in slow and incomplete displacement.

9:00am **SS2+EM+TF-WeM4 Thermal Treatment of Glutamic Acid Etched Ni Nanoclusters on Au{111} Leads to the Formation of 1-D Metal Organic Co-Ordination Networks**, *A.G. Trant, T.E. Jones*, ***C.J. Baddeley***, University of St Andrews, UK

The adsorption of glutamic acid onto 2-D Ni clusters on Au{111} has been investigated using reflection absorption infrared spectroscopy (RAIRS) and scanning tunnelling microscopy (STM). Adsorption at 300 K leads to two distinct adsorbate species which we conclude are zwitterionic species adsorbed either at Ni-like sites in the centre of the clusters or at interfacial sites at the edges of clusters. Adsorption of (S)-glutamic acid causes the complete destruction of clusters of initial diameter <3 nm. We conclude that the Ni islands have been corroded resulting in the formation of a Ni salt - presumably nickel (II) glutamate. On annealing to 350 K, chains of 1-D molecular features are observed in STM experiments. We discuss the possible composition and structure of this salt and conclude that the chains most likely consist of nickel (II) pyroglutamate. Metal pyroglutamate salts are known to be produced by heating glutamate salts. The intermolecular bonding and azimuthal alignment of the 1-D chains are discussed. We also report the formation of analogous networks from Ni + (R)-glutamic acid and discuss the influence of stereochemistry on the structure of the networks.

9:20am **SS2+EM+TF-WeM5 Crossover from Site-Sensitive to Site-Insensitive Adsorption of the Fullerene Derivative PCBM on Au(111) due to Hydrogen-Bond Formation**, ***D. Ecija***, *R. Otero*, Univ. Autonoma de Madrid, Spain, *L. Sanchez*, Univ. Complutense de Madrid, Spain, *J.M. Gallego*, Inst. de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *Y. Wang, M. Alcami, F. Martin*, Univ. Autonoma de Madrid, Spain, *N. Martin*, Univ. Complutense de Madrid, Spain, *R. Miranda*, Univ. Autonoma de Madrid, Spain

The 2D arrangement of organic adsorbates at solid surfaces results from a combination of non-covalent intermolecular forces with molecule-substrate interactions. It is generally thought that molecule-substrate interactions determine adsorption geometry and conformation in first place, while intermolecular interactions affect the subsequent self-assembly of the adsorbates. Only when the molecules can form strong directional bonds, like hydrogen bonds or coordination bonds, and the corrugation of the adsorption potential energy is small, the supramolecular structure is dominated by intermolecular interactions. On the other end of the spectrum, vicinal or heterogeneous surfaces show a strong selectivity in the adsorption site of the adsorbates, leading to a final morphology which is almost exclusively substrate-controlled (templated growth). Usually, the role of molecule-substrate interactions on self-assembly is discussed at the single-molecule level, but this is strictly speaking just an approximation, since the formation of intermolecular bonds might modify the adsorption geometry and thus molecule-substrate interactions. For systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. By means of variable-temperature Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations, here we investigate the crossover from site-selective to site-insensitive adsorption of PCBM, a C60 derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. Whereas at low coverages PCBM self-assembly is dictated almost exclusively by the substrate-related preference for nucleating at the fcc sites of the reconstruction, with a selectivity close to 100%, at higher coverages intermolecular interactions take over the substrate influence, giving rise to PCBM islands that extend through fcc, hcp and dislocations of the herringbone reconstruction. Comparison with theoretical calculations offers the following picture of this crossover: at high-enough coverages hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nano-scale patterns on adsorbed organic overlayers.

9:40am **SS2+EM+TF-WeM6 Nanostructured Binary Molecular Films: Lessons from ACA:C_{60} Mixtures**, ***J.E. Reutt-Robey***, University of Maryland, *B. Xu*, Yanshan University, China, *C.G. Tao*, University of Maryland, *D.B. Dougherty*, National Institute of Standards and Technology, *W. Jin*, University of Maryland

Multi-component aromatic molecular films are of increasing interest in photovoltaic technologies and other organic electronic applications. Binary organic films offer the potential to tailor film structure on the nanoscale to optimize device performance through phase selection, domain size, distribution and orientation. A basic understanding of the factors that control structure in binary molecular films is thus important to advance these materials technologies. We report STM-studies of structure evolution in model donor-acceptor systems, such as ACA:C_{60} and Pentacene:C_{60}. Films prepared by sequential physical vapor deposition onto Ag(111) substrates under UHV are monitored directly with an integrated UHV-STM. We demonstrate how ACA:C_{60} film growth conditions can be adjusted to selectively fabricate films that range from phase-separated hexagonal -C_{60} and chain-phase [4 0, 2]-ACA domains to intermixed co-crystalline chiral domains comprised of C_{60}-terminated ACA pinwheels. Films produced with arbitrary composition generally lead to complex multi-phase structures. Predeposited ACA films with single phase structures provide the most effective pathway to single phases of intermixed structures. For example, the intermixed chiral phase is only accessible from the 2-D ACA molecular gas, whereas extended C_{60} chain structures may be accessed only from the dimer-phase [12 2, 6 5]-ACA domains. We apply lessons from the ACA:C_{60} system to Pentacene:C_{60}, mixtures, utilizing the 2-D pentacene gas to access an intermixed honeycomb Pentacene:C_{60} phase.

10:40am **SS2+EM+TF-WeM9 Detection of Gaseous Nitric Oxide Using X-ray Photoelectron Spectroscopy**, ***M. Dubey***, *J. Schwartz, S.L. Bernasek*, Princeton University

Detection of gaseous nitric oxide (NO) in biological systems has attracted significant attention since the identification of NO as the endothelial-derived relaxing factor (EDRF).[1] NO also acts as a signal molecule in the nervous system, and is associated with the presence of infection and Alzheimer's and other diseases. Apart from biological systems, NO is a main product released on the pyrolysis of nitro-organic explosives. For these reasons, much work has been done in the field of NO detection, and the need for a sensitive detector is evident. In this study, we report a direct and a highly sensitive technique to detect gaseous NO using X-ray Photoelectron Spectroscopy (XPS). The binding of NO by heme proteins is well understood,[2] and we have utilized it for detection. We have developed a reliable method to grow Self-Assembled Monolayers (SAMs) of alkylphosphonic acids on oxide surfaces.[3] This platform is used to covalently attach a uniform layer of an iron heme-like molecule, which was synthesized separately. Differential charging in XPS has been used to ascertain the uniformity of the organic film.[4] The N1s signal from the heme ligand was measured by XPS before and after exposure to NO. Before NO binds to the iron, a single nitrogen peak is present, attributed to the nitrogens of the porphyrin ring. After reaction with NO, a new, distinct peak was observed in the high resolution N1s spectrum. This peak is at a higher binding energy (approx 5.5 eV), and is attributed to the NO bound to the iron. An estimate of the bound NO was calculated using XPS and QCM to be about 40 picomoles.

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11:00am **SS2+EM+TF-WeM10 An In Situ EC-STM Study of the Restructuring of Self-Assembled Monolayers upon Metal Deposition**, ***C. Silien***, *M. Buck*, University of St Andrews, UK

The combination of electrochemistry and self-assembled monolayers offers interesting opportunities for nanotechnology due to high resolution defined by patterned SAMs and simplicity and scalability afforded by electrochemistry. However, control of processes such as electrochemical metal deposition on the nanometer length scale requires exact knowledge of the mutual influence of a SAM structure and electrochemical processes. Aiming for an understanding at the molecular level we report an investigation of the underpotential deposition of copper on Au(111) electrodes modified by ω-(4'-methyl-biphenyl-4-yl)-alkanethiols ($H_3C-(C_6H_4)-(C_6H_4)-(CH_2)_nSH$, BPn). As reported recently, this class of molecules gives rise to pronounced structural variations with length n of the alkane spacer and, for n = even, exhibits polymorphism.[1,2] Furthermore they can be prepared to an exceptionally high structural perfection. These properties make SAMs of BPn thiols an attractive basis for further tailoring of properties of functionalized electrodes and the electrochemical generation of nanometer-scaled structures. A decisive step in SAM controlled electrometallisation is the deposition of the first layer of metal which takes place in the underpotential region. Its understanding is of crucial importance as this layer forms at the SAM-substrate interface and, therefore, affects the properties of the system. Our in situ STM investigations of the underpotential deposition reveal, firstly, pronounced differences between BPn SAMs and alkane thiols and, secondly, a pronounced influence of the length of the alkane spacer in the BPn SAMs, i.e., whether n = odd or even. The molecular resolution achieved in this study combined with time resolved monitoring of the events occurring in the course of the copper deposition allows us to highlight the relationship between the SAM structure and its influence on the generation of nanometer scaled structures by electrochemical metal deposition.

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11:20am **SS2+EM+TF-WeM11 Irradiation-Promoted Exchange Reaction: A New Approach to the Fabrication of Heterogeneous Self-Assembled Monolayers and Chemical Lithography**, ***N. Ballav***, *T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can undergo an exchange reaction with the molecules capable of building a SAM on the same substrate upon the immersion into the respective solution. However, for most systems, the exchange reaction is very slow and incomplete at normal conditions, taking from days to weeks and occurring to a limited extent only. Using several different model systems, we show that the rate and extent of the exchange reaction can be significantly enhanced and even precisely tuned by either electron irradiation with a small dose or exposure to UV light. We assume that both electron and UV irradiation result in the appearance of structural and chemical defects in the target SAM, which promote the molecular exchange. The effect of irradiation and the parameters of the exchange reaction were monitored in detail and correlated with each other using several complementary experimental techniques. The developed approach, irradiation-promoted exchange reaction, can be considered as a platform for the preparation of heterogeneous mixed SAMs. Also, in combination with e-beam or UV-lithography, this method can be used for the fabrication of chemical patterns, including gradient ones. In this regard, the approach is similar to conventional photography: a desired pattern is initially written by electron or UV beam and later "developed" upon its immersion into the solution of a molecular substituent. There are no principal limitations for the form of the fabricated features while the characteristic length scale can be varied in a broad range from centimetres to several tens of nanometers.

11:40am **SS2+EM+TF-WeM12 Calcium Adsorption on Regioregular Poly(3-hexylthiophene): Synchrotron Radiation Photoemission and Microcalorimetric Studies**, ***J.F. Zhu***, *W. Zhao, W.H. Zhang,* University of Science and Techonology of China*, J. Farmer, C.T. Campbell*, University of Washington

The adsorption of Ca on the regioregular poly(3-hexylthiophene) (rr-P3HT) thin film surfaces at 300 K has been studied using synchrotron radiation photoemission spectroscopy, adsorption microcalorimetry and atomic beam/surface scattering. The polymer films were spin-coated on the Si wafers with typical thickness of > 100 nm and were free of oxygen contamination as clarified by both X-ray photoelectron spectroscopy and Auger electron spectroscopy. Synchrotron radiation photoemission spectroscopy provides precise experimental information on the alteration of the Ca/polymer interfacial energy level line-up and the chemical nature at this interface. The deposition of calcium on the rr-P3HT film at room temperature induced a decrease of the work function, indicating Ca donates electron density to the polymer substrate. Moreover, Ca adsorption led to the depression of the bands of the rr-P3HT. The strength of interaction between Ca and the rr-P3HT is probed by both microcalorimetric heats of adsorption and sticking probability measurements.

12:00pm **SS2+EM+TF-WeM13 Supramolecular Coordination Networks at Surfaces: Self-selection and Error Correction in Multi-ligand Nanopore Arrays**, ***S.L. Tait***, *A. Langner, N. Lin,* Max Planck Institute for Solid State Research, Germany*, C. Rajadurai, M. Ruben,* Research Center Karlsruhe, Germany*, K. Kern*, Max Planck Institute for Solid State Research, Germany and Ecole Polytechnique Fédérale de Lausanne, Switzerland

Supramolecular self-assembly of organic ligands and metal centers is a topic of growing interest for efficient molecular-scale patterning of surfaces. Molecular networks can be designed to self-organize in regular, 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligands. This approach offers a natural alternative to current nano-fabrication methods, allowing atomic and molecular building blocks to organize themselves into useful nanostructures, and is a model system for supramolecular and biomolecular assembly in general. We present recent results of self-assembled supramolecular networks on the Cu(100) surface, which demonstrate multi-ligand construction of 2D arrays of compartments with tunable shape and size. These binary combinations of complementary ligands represent a significant step in complexity over previous studies. Of technological interest is the capability for modular replacement of either of the two ligands to produce a range of nanopore lattice sizes and shapes in a very predictable and programmable way. Of more fundamental interest in these systems is molecular level resolution imaging using scanning tunneling microscopy, which allows an unprecented perspective of fundamental steps to supramolecular assembly, such as structural error correction achieved by efficient molecule self-selection. Non-covalent metal—organic coordination provides room temperature stability and high structural ordering through directional and selective interactions, but also allows for bonding reversibility, enabling error correction during assembly. By selection of molecular building blocks with specific properties, we can "program" these systems to pattern a surface with homogenous networks of specific size, structure, and physical and chemical properties. The ability to tailor the size and functionality of nanometer-scale arrays produced by molecular self-assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, thin film growth, and other fields.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+TF+SS-WeA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: J.S. Lewis, RTI International

1:40pm **EN+TF+SS-WeA1 ENABLE-based Low Temperature Growth of In-rich InGaN Films**, ***T.L. Williamson**, M.A. Hoffbauer,* Los Alamos National Laboratory, *N. Miller, R.E. Jones, K.M. Yu,* Lawrence Berkeley National Laboratory, *P. Flanigan, J. Wu,* University of California, Berkeley, *J.W. Ager, Z. Liliental-Weber, E.E. Haller, W. Walukiewicz*, Lawrence Berkeley National Laboratory

The different optimum growth temperatures for the group III-nitride compounds (e.g. GaN >900C and InN ~550C) make the growth of In-rich and fully compositionally graded InGaN films by MOCVD or MBE a considerable technological challenge. Recently, energetic neutral atomic-beam lithography & epitaxy (ENABLE) has been developed at LANL that makes possible isothermal low-temperature growth of high-quality GaN and $In_xGa_{1-x}N$ alloys over the entire composition range (0<x<1). ENABLE uses a large flux of neutral nitrogen atoms to activate surface chemical reactions, thereby mitigating the need for high substrate temperatures and allowing the growth of high quality III-nitrides at substrate temperatures far below those of other conventional techniques (<600C) at rates exceeding 2 microns/hr. We will present recent results for ENABLE-grown InN and In-rich InGaN showing spectroscopic, X-ray diffraction, Rutherford backscattering spectrometry (RBS), transmission electron microscopy, and Hall effect measurements to assess the thickness, composition, crystalline quality, and optical and electrical properties of the films. InN films show intense luminescence at the bandgap of ~0.7 eV with electron mobilities exceeding 700 cm^2/ V·sec. We will also present characterization results for compositionally graded films grown from pure GaN and grading to InN and from pure InN and grading to GaN. These results establish ENABLE as a new technique uniquely capable of growing InGaN films of widely varying composition including compositionally graded InGaN films and InN/GaN heterostructures.

2:00pm **EN+TF+SS-WeA2 Tandem-Junction Solar Cells using BeTe Buffer Layers for AlGaAs Molecular Beam Epitaxy on Silicon Substrates**, ***K.P. Clark**, E. Maldonado, F. Amir, W.P. Kirk*, University of Texas at Arlington

Monolithically-stacked tandem-junctions allow solar cells with conversion efficiencies above the single-junction limit. An optimal bandgap combination of 1.7 eV and 1.1 eV has a theoretical efficiency above 30% for a series-connected cell. Aluminum gallium arsenide epitaxially grown on silicon is a natural implementation, but has long-standing crystal-quality challenges due to lattice mismatch, thermal expansion mismatch, and island growth of AlGaAs. We report investigations of AlGaAs molecular beam epitaxy on prelayers of the wide-bandgap II-VI compound beryllium telluride BeTe on arsenic-passivated silicon. AlGaAs is nearly lattice matched to BeTe but has a strong tendency for island formation, which is suppressed by low-temperature growth initiation. $Al_{0.15}Ga_{0.85}As$-GaAs multiple quantum-well p-i-n junction structures were processed and characterized electrically under illumination. The short-circuit photocurrent J_{SC} and open-circuit voltage V_{OC} for the Si/BeTe based junction approach within 15% and 30% respectively of those for a similar junction grown on a GaAs substrate. We report techniques for initial AlGaAs growth including solid-phase epitaxy, BeTe termination, and germanium adlayers studied using RHEED diffraction, X-ray diffraction, and transmission electron microscopy.

Supported in part by NASA.

2:20pm **EN+TF+SS-WeA3 Gaseous Deposition of Lead Sulfide Nanoparticle/Ti-Phthalocyanine Composite Films**, *I.L. Bolotin, D.J. Asunskis, A.M. Zachary, **A.T. Wroble**, L. Hanley*, University of Illinois at Chicago

Composite materials composed of inorganic semiconductor nanoparticles (NPs) dispersed in organic matrices may find use in photovoltaics, photodiodes, nonlinear optical devices, and other applications. This interest arises from the possibility of tuning the optoelectronic properties of the composite by varying the NP size and concentration within the organic matrix. Bulk PbS is a group IV–VI semiconductor with a narrow band gap of 0.41 eV at room temperature. Strong quantum size effects occur for <20 nm PbS NPs. Among the other potential advantages of PbS NPs is their high electron affinity, which will enhance charge transfer from an intermingled organic phase. Most of the lead salt NP photovoltaics devices produced to date have been prepared from the solution phase using colloidal techniques. However, gaseous deposition techniques possess certain advantages for the synthesis of nanocomposites: it is inherently suited to film deposition, is compatible with traditional methods of fabricating semiconductor devices, allows control of oxidation during deposition, and it can reduce the agglomeration of NPs. This work demonstrates that gaseous deposition can synthesize a composite film with <5 nm diameter PbS NPs of narrow size distribution embedded within a titanyl phthalocyanine (TiPc) organic matrix. Composite film samples were fabricated here using a cluster beam deposition source combining magnetron DC-sputtering and gas-agglomeration techniques in a fashion similar to that originally developed by Haberland and coworkers. X-ray photoelectron spectroscopy showed that PbS was successfully incorporated into the TiPc matrix during co-deposition. Transmission electron microscopy (TEM) was used measure the size, shape, distribution, and crystallinity of the NPs in these composite films. Soft-landing of PbS clusters into the TiiPc organic matrix allowed the clusters to maintain their three-dimensional structure upon deposition. In the absence of the TiPc matrix, PbS showed the aggregation into much larger, irregularly-shaped particles. PbS NPs appeared homogeneously distributed in the TiPc matrix, with particle spacings of several times the particle diameter. TEM also showed that at least some NPs deposited into TiPc were crystalline. This method also allows for deposition of composite films composed of any evaporable organic and inorganic nanoparticles that can formed by sputtering and reaction within the cluster source.

2:40pm **EN+TF+SS-WeA4 Plastic Bulk-Heterojunction Solar Cells and Near-Infrared Photodetectors**, *G. Li, Y. Yao,* University of California, Los Angeles, *L. Yu, Y. Liang, S. Xiao,* University of Chicago, ***Y. Yang***, University of California, Los Angeles **INVITED**

Polymer based solar cells and photodetectors have tremendous application in harnessing solar energy and photodetection in a cost-effective way. Here we studied the self-organization effect in polymer solar cells and first demonstrated plastic near-infrared photodetectors using low band-gap polymer. The self-organization effect in polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is studied in an evolutional way, with the difference being spin-coating time ts (20 to 80 sec) which controls solvent annealing time (ta) by the solvent residue. Photoluminescence (PL), ultraviolet-visible (UV-vis) absorption spectroscopy, scanning atomic force microscopy (AFM), and grazing-incidence X-ray diffraction (GIXD) were conducted on these blend films and linked to the device performance. In addition to the high performance polymer solar cells, we also demonstrated a fast response near-infrared detector using a new low band gap material. With promising results shown in this presentation, we believe the low band gap materials will open up a new perspective in near-infrared detection.

4:00pm **EN+TF+SS-WeA8 Defect Characterization of CdTe and CdMgTe Solar Cells and Their Correlation to the Device Properties**, ***R.G. Dhere**, D. Young, J. Scharf, A. Duda, B. To, R. Noufi*, National Renewable Energy Laboratory

CdTe solar cells are at the forefront of commercial thin-film solar cells because of the high laboratory efficiencies and relative ease of fabrication. The current losses for these devices are well understood, with very small room for improvement. On the other hand, open-circuit voltage (V_{oc}) of champion devices is much lower than its potential and presents the only path to improve device performance. In this paper, we present our work on the CdTe and CdMgTe devices fabricated by close-spaced sublimation and physical vapor deposition on glass/SnO_2/CdS substrates. The devices are heat-treated in chloride vapor after deposition, in a controlled ambient, in temperature range of 390°-440°C. The treatment results in recrystallization of the samples deposited at low temperature (~400° C) and selective recrystallization at the CdS/CdTe interface in samples deposited at higher temperatures. The post-deposition treatment also improves the electronic properties of the absorber due to reduced defect density and results in improved device performance. Our investigation studies the effect of bandgap variation and defect density within the space-charge region in the absorber on the device properties, particularly V_{oc}. The bandgap of the alloy is varied by changing the alloy composition of CdSTe alloy formed at the CdS/CdTe interface and CdMgTe alloy composition. We examine the bandgap range of 1.45-1.65 eV for the absorber layer. We have varied defect density in the absorber layer by adjusting the substrate temperature and degree of post-deposition chloride treatment. The structural properties of the samples are studied by atomic force microscopy. The devices have been characterized using drive-level capacitance profiling in combination with capacitance-voltage analysis, in addition to conventional photovoltaic analysis. We will present the data on the devices with a wide range of performance and investigate the correlation between device parameters and the material properties such as bandgap and defect density. This abstract is subject to government rights.

4:20pm **EN+TF+SS-WeA9 Electron Backscatter Diffraction of CdTe Thin Films - Effects of CdCl2 Treatment**, ***H.R. Moutinho***, *R.G. Dhere, C.-S. Jiang, B. To, M.M. Al-Jassim*, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) utilizes the electron beam of a scanning electron microscope (SEM) to investigate the crystallographic orientation of materials with high spatial resolution. In EBSD, some of the electrons of the SEM beam are diffracted by the crystalline planes of the sample and collected by a detector, where they form a pattern of Kikuchi lines. These patterns are characteristic of the crystal structure and orientation, and they are collected while the electron beam is being scanned, forming maps of crystallographic orientation. In contrast to X-ray diffraction, which gives the crystallographic orientation of a macroscopic volume of the bulk sample, EBSD provides the individual orientation of volumes with nanometer dimensions. To optimize the EBSD signal, the sample must be inclined by about 70° in relation to the electron beam. Consequently, in rough samples, topographic features shadow some of the diffracted electrons from reaching the detector; thus surface preparation is a common requirement. In this work, we describe the surface processing of CdTe thin films deposited by close-spaced sublimation and physical vapor deposition (PVD). Most of the films studied were too rough to produce good EBSD data. Polishing flattened the sample, but created an amorphous layer on the surface, resulting in no diffraction patterns. Ion-beam milling was not as effective in flattening the surface, but removed rough surface features, resulting in high-quality EBSD data. Etching and light ion milling after polishing also produced good results. After optimizing the sample preparation process, we studied PVD CdTe samples after $CdCl_2$ treatment using dipping or vapor processes, with different parameters. We observed a striking difference in the sample microstructure depending on the $CdCl_2$ process and parameters–with grain sizes varying from a few to several dozen micrometers. Our results showed that maintaining a steady source of $CdCl_2$ during the treatment, compared to a fixed amount, results in completely different recrystallization dynamics. We also studied the grain structure from the substrate to the surface by doing EBSD in cross sections of the samples, as well as analyzing samples after different degrees of polishing.

4:40pm **EN+TF+SS-WeA10 Effect of Selenization Temperature on the Grain Growth of Absorber Layer in Ultra Thin CIGS/CdS Solar Cells**, ***S.A. Pethe***, *N.G. Dhere*, Florida Solar Energy Center

Solar cells based on $CuIn_xGa_{1-x}Se_2$(CIGS) have achieved efficiencies of 19.5% and therefore are promising candidates for economic, large-scale production. CIGS thin film solar cells having absorber thickness of 2.5 µm have shown good performance. However, CIGS being a direct bandgap material, theoretically efficient cells could be prepared with absorber thickness as low as 0.5 µm. The rationale behind decreasing the CIGS thickness is to reduce consumption of the scarce and costly resource, indium. It has been observed that the performance of the solar cells degrades as the thickness goes below 0.75 µm. 0.9 µm thick absorber layer are prepared at PV Mat Lab facility at Florida Solar Energy Center (FSEC) with device conversion efficiency of 6.26% as measured at FSEC. The reason for this degradation can be attributed to the defects in the bulk of the absorber material. We know from the Movchan&Demchishin zone model that the rate of grain growth becomes almost negligible once the grains with favored texture and orientation have consumed all the unfavorable grains. This results in columnar grain structure with parallel boundaries. Similar grain structure was observed for the CIGS absorber layers with thickness of about 2.5 µm. It was observed that the grains were finer towards the back contact and larger at the surface and as the thickness goes on reducing there is not enough material for the grains to grow and coalesce. This results in smaller grains and so larger grain boundaries. Another factor affecting the grain size is the mobility of the deposited species which can be increased by increasing the annealing temperatures during selenization. But in case of ultra thin film absorber layer the higher temperatures adversely affect the molybdenum back contact layer thus introducing higher series resistance issues. Hence, in case of ultra thin CIGS absorber layer the selenization time - temperature profile needs to be optimized to obtain a favorable columnar grain structure. The material characterization of the different absorber layers will be carried out using scanning electron microscopy and transmission electron microscopy. The absorber layers would be further fabricated on to complete the device and current-voltage characteristics would be carried out to understand the effect of different temperature-time profiles on the device parameters such as open circuit voltage, short circuit current, fill factor and finally the conversion efficiency.

5:00pm **EN+TF+SS-WeA11 Thin Film Epitaxial Growth of $CuInSe_2$ Bicrystals for Grain-Boundary Studies**, ***A.J. Hall***, *D.N. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Photovoltaics based on $CuInSe_2$ and related materials have the highest performance of any thin film devices. The nature and role of grain-boundaries in $CuInSe_2$ devices is currently poorly understood. Previous studies on the influence of grain-boundaries in $Cu(In,Ga)Se_2$ devices have shown that they exhibit little to no detrimental effect on photovoltaic device performance. Polycrystalline $CuInSe_2$ devices currently outperform single crystal $CuInSe_2$ devices. Past studies have been focused on average electrical properties or local surface electrical measurements for observation of the influence of boundaries on film properties. Since polycrystal devices have crystal sizes on the order of 1 micron, optoelectrical measurements are difficult. In order to alleviate these difficulties, a single high-angle grain-boundary in epitaxial $CuInSe_2$ has been grown on a GaAs bicrystal substrate using a hybrid sputtering and evaporation technique. Electron backscatter diffraction and x-ray diffraction show that film growth is epitaxial across all boundaries (high-angle and twin) in the bicrystal substrates. Atomic force microscopy, profilometry, and focused ion beam cross-sectioning results indicate that surface polarity and termination have a strong influence on film thickness and morphology. Near grain boundary morphology suggests mass transport leading to boundary migration is occurring. It is proposed that high surface energy anisotropy (on the opposing $\{111\}_{A,B}$ surface facets) motivates mass transport during the growth of $CuInSe_2$ at crystal boundaries.

Surface Science

Room: 608 - Session SS1-WeA

Reactions on Metal Surfaces

Moderator: A.J. Gellman, Carnegie Mellon University

1:40pm **SS1-WeA1 Thermally Induced Oxidation and Decomposition Products from NCO /Cu(001)**, ***E.Z. Ciftlikli***, *A.V. Ermakov, J. Lallo, S. Rangan, I.G. Shuttleworth, E.Y.-M. Lee, B.J. Hinch,* Rutgers, The State University of New Jersey, *S.D. Senanayake*, Oak Ridge National Laboratory

We report on high-resolution quantitative XPS studies, and complementary NEXAFS and TPD studies of adsorbed isocyanate (NCO) species on Cu(001). Adsorbed NCO can be prepared by room temperature dissociative adsorption of isocyanic acid (HNCO).[1] XPS and NEXAFS confirm that, following hydrogen desorption, solely NCO remains. This is stable to at least 473K. However this species is prone to oxidation from any coadsorbed atomic oxygen. At temperatures as low as 373K, quantitative XPS results indicate CO_2 desorption, while the surface N concentration is conserved. NCO oxidation to adsorbed nitrogen and CO_2, continues until the atomic oxygen is depleted. This chemistry, while observed over a wide range of initial O surface coverages, is however modified in the presence of CN coadsorbates. We have also prepared NCO containing surfaces, through room temperature O_2 and C_2N_2 exposures. Under these conditions, conversion of O and adsorbed CN, to NCO, is substantial though not complete, i.e. the resulting surface hosts NCO, CN and O species. These surfaces, on annealing to 373K again demonstrate N atom production but now also, in large part, CO desorption. This apparently direct NCO decomposition, to $N_{(a)}$ and CO, is observed only in the presence of coadsorbed $O_{(a)}$ and $CN_{(a)}$. At temperatures in excess of 573K, another thermally activated process is observed that is in common to both isocyanate containing surface types; i.e. those prepared with HNCO exposure or $O_2 + C_2N_2$ exposures. In this latter process any coadsorbed CN appears to be only a passive bystander. We discuss possible mechanisms for these thermally activated reactions, and implications of these chemistries on other more catalytic surfaces commonly used for NO_x reduction.

[1] H. Celio, K. Mudalige, P. Mills, M. Trenary, Surface Science 394 (1997) L168-L173.

2:00pm **SS1-WeA2 Nano-Structural Information Carried by Desorbing Products; Surface-Nitrogen Removal and Angular Distributions**, ***T. Matsushima***, Hokkaido University, Japan **INVITED**

Angle-resolved (AR) product desorption analysis assigns active surface species directly emitting products. Its application is limited to products with hyper-thermal energy. This paper delivers the analysis of surface-nitrogen removal processes in both the thermal decomposition of adsorbed N2O and steady-state NO reduction on Rh(100), Rh(110) and Pd(110), in which desorbing nitrogen holds high kinetic energy. In the thermal decomposition of N2O(a) on Rh(100), N2 desorption shows two peaks at around 85 K and 110 K. At low N2O coverage, the desorption at 85 K collimates at about 66 degrees off normal toward the [001] direction, whereas at high coverage, it sharply collimates along the surface normal. In the steady-state NO+D2 reaction on Rh(100), the N2 desorption preferentially collimates at around 71 degrees off normal toward the [001] direction at 550-700 K, whereas it collimates predominantly along the surface normal at higher temperatures. At lower temperatures, the surface nitrogen removal in the NO reduction is due to NO(a)+N(a) to N2O(a) to N2(g)+O(a), whereas, at higher temperatures, the associative desorption of nitrogen adatoms is predominant. This NO reduction mechanism is also operative on Rh(110) and Pd(110) with different contributions from the two pathways. The emission angle of nascent N2 is controlled by the orientation of adsorbed N2O and the collimation angle of desorbing N2 is also affected by co-adsorbed species. In the steady-state N2O+D2 reaction on Rh(110), the N2 desorption collimates closely along the [001] direction (close to the surface parallel) below 340 K and shifts to ca. 65 degrees off normal at higher temperatures. In the reduction with CO, the N2 desorption collimates along around 65 degrees off normal toward the [001] direction above 520 K, and shifts to 45 degrees at 445 K with decreasing surface temperature. In this temperature range, adsorbed CO increases and scatters the product N2.

2:40pm **SS1-WeA4 Reactivity of Atomic Oxygen on Gold Surfaces**, ***J.L. Gong****, *R.A. Ojifinni, J.M. White, C.B. Mullins*, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated by employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions.We demonstrate that ammonia does not dissociate on the clean Au(111) surface but adsorbed O atoms, O_{ad}, facilitate $NH_{3,ad}$ decomposition. The selectivity of the catalytic oxidation of ammonia to N_2 or to NO on Au(111) is tunable by the amount of atomic oxygen precovering the surface. Both N_2 and NO are likely formed via simple recombination reactions (N_{ad} + N_{ad} and N_{ad} + O_{ad}). At low oxygen coverages ($\theta_O < 0.5$ ML) (1 ML of oxygen is defined as 1.387 x 10^{15} atoms/cm^2 and refers to a single atomic layer of close-packed gold), adsorbed ammonia is stripped to NH_x ad which decomposes to form gaseous N_2. At high O_{ad} coverages, NO is formed in a surface reaction between N_{ad} and O_{ad}, but most surface N species involved recombine to form N_2 which desorbs with a peak at ~ 460 K. Higher yields of N_2 can be obtained if the O_2/NH_3 mix is kept NH_3 rich. We also present results of low-temperature CO oxidation and the role of moisture on an atomic oxygen covered Au(111) surface. The effect of atomic oxygen precoverage on CO oxidation was examined at sample temperatures as low as 77 K. Prompt CO_2 production was observed when the CO beam impinges on the sample followed by a rapid decay of CO_2 production in all cases. At oxygen precoverages above 0.5 ML, the initial CO_2 production decreases with increasing oxygen precoverage primarily due to the decrease in CO uptake. CO oxidation at 77 K goes through a precursor mediated reaction mechanism, where CO is in a precursor or trapped state and oxygen atoms are in a chemisorbed state. The role of adsorbed water was studied by using isotopically labeled water [$H_2{}^{18}O$] to distinguish the oxygen species from that used in oxygen atom exposures [^{16}O]. Evidence is presented that shows activated water or OH groups formed from water can directly participate in oxidizing CO on an atomic oxygen covered Au(111) surface.

3:00pm **SS1-WeA5 Abstraction of ^{18}O Atoms Chemisorbed on Pd(111) by ^{16}O Atoms Incident from the Gas-Phase**, ***H.H. Kan***, *R.B. Shumbera, J.F. Weaver*, University of Florida

We investigated the reactions of gas-phase ^{16}O atoms with ^{18}O atoms initially chemisorbed on the Pd(111) surface using direct product monitoring and temperature programmed desorption. We find that $^{16}O^{18}O$ molecules desorb promptly at surface temperatures as low as 100 K during the atom-surface collisions, which suggests that ^{18}O abstraction occurs by a direct reaction with incident ^{16}O atoms. Only about 20% of the initially adsorbed ^{18}O evolves as $^{16}O^{18}O$ during the beam exposures, independent of the surface temperature from 100 K to 500 K. At all temperatures, the $^{16}O^{18}O$ desorption rate initially rises to a maximum and decays thereafter with increasing beam exposure. Above 200 K, a second maximum in the desorption rate also appears after longer exposures, with the intensity of this maximum increasing with increasing surface temperature. We find that the abstraction kinetics is primarily determined by the distribution of oxygen phases that develop on the surface during oxygen uptake from the beam. Specifically, the data suggests that the observed $^{16}O^{18}O$ desorption arises from direct reactions between gaseous ^{16}O atoms and ^{18}O atoms chemisorbed either on the bare metal or on top of a surface oxide, and that the abstraction of oxygen atoms incorporated within both surface and bulk oxides occurs with low probability. As a result, only a fraction of the ^{18}O atoms are abstracted before incorporating into oxide phases during the beam exposure. The second maximum in the $^{16}O^{18}O$ desorption rate is attributed to abstraction of ^{18}O atoms chemisorbed on top of a developing surface oxide. The increase in this rate maximum with increasing surface temperature will be discussed within the context of an exchange process between oxygen atoms within the surface oxide and oxygen atoms chemisorbed on top of the surface oxide, and a kinetic analysis of the exchange will be presented.

4:00pm **SS1-WeA8 An In Situ Investigation of Hyperactive States for CO Oxidation on Platinum Group Metal Catalysts**, ***Y. Cai***, *Z. Yan, K.K. Gath, M.S. Chen*, Texas A&M University, *D.W. Goodman*, Texas A&M Universtiy

The oxidation of carbon monoxide on platinum group metal catalysts has been studied for decades due to its technological importance in pollution control and fuel cells.[1-3] Ru catalysts were found to have dramatically different activities at ultrahigh vacuum compared with elevated pressure conditions. The formation of 1 monolayer (ML) surface oxide layer is believed to give rise to the much higher activity of Ru catalysts under high pressure conditions.[4] On the other hand, at stoichiometric reaction conditions, similar activation energies and kinetic orders were found for supported Pd, Pt, Rh and Ir catalysts at high and low pressure conditions.[3] Recent studies have shown that there are hyperactive states on Pd, Pt and Rh catalysts, with the CO_2 formation rate per metal atom site per second (turnover frequency, TOF) reaching into the thousand's, two orders of magnitude higher than the rate measured at stoichiometric reaction conditions. This hyperactive state takes place on an oxygen-rich surface at a well-defined O_2/CO ratio and specific temperature for each metal. The oxygen adsorption energies for Pt, Pd, Rh and Ru correlate directly with the O_2/CO ratio required to achieve the hyperactive catalytic state. PM-IRAS is used to investigate in situ the surface species under reaction conditions. The thickness and chemical nature of the surface oxygen layer giving rise to the hyperactive state is explored with XPS.

[1]. T. Engel and G. Ertl, Adv. Catal. 28 (1979) 1

[2]. J.E. Turner, B.C. Sales, and M.B. Maple, Surf. Sci. 109 (1981) 591

[3]. P.J. Berlowitz, C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 92 (1988) 5213

[4]. C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 90 (1986) 1360.

4:20pm **SS1-WeA9 Imaging of Transition Metal Oxidation and Catalysis**, ***J.I. Flege***, *P. Sutter*, Brookhaven National Laboratory

Transition metals have attracted significant attention because of their high activity in oxidation catalysis. For several materials this activity is due to the formation of thin oxides under reaction conditions. The most prominent example of this type of activation is Ru(0001), which only turns into an excellent low-temperature oxidation catalyst at higher oxygen partial pressures.[1] Despite extensive efforts in characterizing this and other similar systems, a number of fundamental questions remain unanswered, e.g., regarding the initial oxidation mechanism, the nature of oxygen-rich near-surface structures, and their individual catalytic activities. Here we discuss major progress toward understanding both transition metal oxidation and the catalytic activity of the resulting oxygen-rich structures, made possible by a novel spectroscopic imaging technique: dynamic intensity-voltage low-energy electron microscopy (dIV-LEEM). In contrast to IV low-energy electron diffraction (IV-LEED), dIV-LEEM produces spectroscopic stacks of real-space images of a surface as a function of electron acceleration voltage. Hence, the technique combines the real-time nano-imaging capabilities of conventional LEEM with the structural sensitivity of IV-LEED, making it possible to obtain, for instance, local time-dependent IV-LEED characteristics at every image pixel. Combined with dynamic LEED theory, such data can be used to identify nanoscale surface phases, for real-time structural fingerprinting of complex structural transitions, and to explore cooperative effects in surface reactions. Specifically, we establish the pathway of initial oxidation of the 4d late transition metals. The initial oxidation of Ru(0001), for instance, was predicted to proceed via the formation of a thin surface oxide as a precursor to the RuO_2 bulk oxide.[2] Our dIV-LEEM movies show instead that bulk and surface oxides grow simultaneously without transforming into one another. This finding has far-reaching consequences for catalysis, which will be discussed on the basis of real-time dIV-LEEM movies during the catalytic cycle.[3] Strikingly, the coexistence of several nanoscale structures induces cooperative effects that may be visualized and quantified by dIV-LEEM analysis.

[1] H. Over et al., Science 287, 1474 (2000).

[2] K. Reuter et al., Chem. Phys. Lett. 352, 311 (2002).

[3] J. I. Flege and P. Sutter, submitted (2007).

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* Morton S. Traum Award Finalist

4:40pm **SS1-WeA10 Multisite Lattice-Gas Modeling for Chemisorption and Reaction on Metal(100) Surfaces**, ***D.-J. Liu**, J.W. Evans*, Iowa State University

A multisite lattice-gas model[1] has been developed to provide a realistic description of the chemisorption of single species (CO, O, etc) on the (100) surface of metals such as Rh, Pd, and Ir. In addition, the model describes more complicated chemisorption and reaction processes for mixed adlayers. Population of various adsorption sites must be incorporated for reliable modeling even for single species on a single surface at higher coverages. For reactions such as CO oxidation in mixed layers, distinct local reaction configurations or pathways can contribute to different peaks observed in the temperature-programmed-reaction (TPR) spectra. Thus, our general multisite lattice-gas model allows populations of different adsorption sites (e.g., bridge, top, and hollow sites) incorporating site-specific binding energy and interactions. Parameters are chosen based on comparison with experimental data and DFT results. In addition, it is necessaary to incorporate very rapid diffusion of the reacting species (with rates many order of magnitude above other rates). We utilize kinetic Monte Carlo simulations to analyze model behavior and to interpret a variety of experimental data (heat of adsorption, TPD, TPR, etc) for the above-mentioned metal surfaces.

[1] D.-J. Liu, J. Phys. Chem. C (2007); D.-J. Liu and J. W. Evans, J. Chem. Phys. 124 (2006) 154705.

5:00pm **SS1-WeA11 Adsorption and Oxidation of SiH$_4$ on Pd(111)**, ***D. Kershner**, J.W. Medlin*, University of Colorado at Boulder

A better understanding of metal-silicon and metal-SiO$_2$ interfaces would be applicable in many areas of study. Due to the buried nature of these interfaces in applications, they have not been well studied. To study these interfaces, a model system consisting of sub-monolayer coverages of silicon containing molecules adsorbed on single crystal metal surfaces has been investigated, using the metal as the substrate rather than the silicon/silica. In this contribution, we report on a multi-technique surface science investigation of silane adsorption and reaction on clean and O-covered Pd(111). Silane adsorption on Pd(100) and other metals has been studied previously.[1-3] These studies found that silane desorbs dissociatively, producing H adatoms and SiH$_X$ adsorbates at cold temperatures, followed by complete dissocation of the surface SiH$_X$ and the formation of a metal silicide phase at higher temperatures. Studies were performed using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and auger electron spectroscopy (AES). SiH$_4$ adsorption resulted in the formation of SiH$_X$ species on the Pd(111) surface stable to ca. 200K. Complete dissociation occurs upon heating, however it is unclear if a silicide is formed due to the lack of splitting in the Si LVV AES peak.[4] Coadsorption of SiH$_4$ and O$_2$ leads to low temperature oxidation of surface Si atoms, forming a layer of SiO$_X$. This is characterized by the presence of Si-O bonds in HREELS spectra and an AES feature at 84 eV.[5] CO adsorption has also been used to probe of the effect of the SiO$_X$ layer on Pd surface chemistry. Density functional theory studies have also been performed to investigate the structures formed during surface silicon oxidation.

[1] M.S. Nashner, J.C. Bondos, M.J. Hostetler, A.A. Gewirth, R.G. Nuzzo, Journal of Physical Chemistry B 102 (1998) 6202-6211.

[2] C.J. Ennis, S.A. Morton, L. Sun, S.P. Tear, E.M. McCash, Chemical Physics Letters 304 (1999) 217-224.

[3] E.M. Mccash, M.A. Chesters, P. Gardner, S.F. Parker, Surface Science 225 (1990) 273-280.

[4] G.Y. Robinson, Applied Physics Letters 25 (1974) 158-160.

[5] C.R. Helms, Y.E. Strausser, W.E. Spicer, Applied Physics Letters 33 (1978) 767-769.

Surface Science

Room: 611 - Session SS2-WeA

Oxide Surface Structure I

Moderator: R.L. Kurtz, Louisiana State University

1:40pm **SS2-WeA1 Diffusion of Bridge-bonded Oxygen Vacancies on TiO$_2$(110)**, ***Z. Zhang**,* Pacific Northwest National Laboratory*, Q. Ge,* Southern Illinois University*, S.-C. Li,* University of Texas at Austin*, B.D. Kay,* Pacific Northwest National Laboratory*, J.M. White,* University of Texas at Austin*, Z. Dohnálek*, Pacific Northwest National Laboratory

Since oxygen atom vacancies play a central role in the behavior of oxide materials, determining their properties is widely pursued both experimentally and theoretically. Rutile TiO$_2$(110) has became a model system for the studies of lattice oxygen defects - bridge-bonded oxygen vacancies (BBO$_V$'s). Despite that, surprisingly little is known about the spatial distribution and/or mobility of these BBO$_V$ sites. As a function of temperature between 340 and 420 K, we report here the first measurements and calculations of the intrinsic mobility of BBO$_V$'s on a rutile TiO$_2$(110) surface. Under conditions where interference by adsorbates was negligible, isothermal atomically-resolved scanning tunneling microscope images that track individual vacancies in real time show that vacancies migrate along bridge-bonded oxygen (BBO) rows. The hopping rate increases exponentially with increasing temperature with experimental activation energy of 1.15 eV. Density functional theory calculations are in very good agreement giving an energy barrier for hopping of 1.03 eV. In agreement with the theory, the BBO$_V$ distribution determined by analysis of the STM images indicates short-range repulsive interactions between vacancies on a given BBO row. 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.

2:00pm **SS2-WeA2 Probing the Structures of CeO$_x$(111) Thin Films and Ceria-Supported Metal Particles with Scanning Tunneling Microscopy**, ***J. Zhou**, A.P. Baddorf, V. Meunier, S.V. Kalinin, S.H. Overbury, D.R. Mullins*, Oak Ridge National Laboratory

Cerium oxide and ceria-supported metal nanoparticles are important heterogeneous catalysts. They exhibit unique chemical reactivity dependent on Ce oxidation state as revealed by our previous XPS and TPD studies. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible (111) oriented thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria films are dependent on the film thickness and the degree of ceria reduction. Hexagonal superlattice structures consisting of five CeO$_2$ unit cells coincident with seven Ru unit cells can be produced when the films are two or three layers thick and disappear with the increase of film thickness. DFT calculations were performed to explain the origin of these superlattice structures. Fully oxidized CeO$_2$(111) film exhibits a fairly low density of point defects due to the formation of O vacancies. However, the number of surface defects increases as the ceria film is reduced. Metal particles (Pd and Rh) were vapor-deposited onto ceria thin films at 300 K. The growth of metal particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state. The research is sponsored by DOE BES Division of Chemical Sciences, Geosciences, and Biosciences.

2:20pm **SS2-WeA3 Structure and Stability of Cerium Oxide Surfaces in an Oxidizing Environment from First-Principles**, *M. Fronzi, A. Soon,* The University of Sydney, Australia*, B. Delley,* Paul Scherrer Institut, Switzerland*, E. Traversa,* University of Rome "Tor Vergata", Italy*,* ***C. Stampfl***, The University of Sydney, Australia

Because of its peculiar and desirable properties, cerium oxide, has been the object of intense interest in relation to solid oxide fuel cells (SOFC) as well as to heterogeneous catalysis, e.g., it can effectively reduce NO$_x$ emissions as well as convert harmful carbon monoxide to carbon dioxide. Since it behaves as a good ionic transporter, and at the same time as a good catalyst, cerium oxide finds application both as an electrolyte and as an anode support in SOFCs. In anode reactions, it plays an active part in the catalysis of the fuel cell, and thus it is important to investigate the properties of the oxide surfaces exposed to an anodic fuel cell gas environment (e.g. methane, CH$_4$). Furthermore, for a particular subclass of fuel cells (single chamber) the anodic side is exposed to oxygen as well as the fuel. For this reasons it is of high importance to understand the behavior of cerium oxide in varying oxygen environments. Using density-functional theory as implemented in the DMol^3 code,[1] we investigate the structure and stability of CeO$_2$ surfaces under realistic conditions using the approach of ab initio atomistic thermodynamics.[2] From calculation of the surface free energy, we obtain the pressure-temperature surface phase diagram. This allows us to identify and predict stable, and potentially catalytically important, structures and stoichiometries under varying pressure and temperature conditions. We investigate many different geometries for the low index (100), (110), and (111) surfaces, including structures containing defects. For a wide range of the oxygen chemical potential we find that the thermodynamically most stable surface is CeO$_2$(111). For increasingly more reducing conditions, surfaces with oxygen vacancies become more stable, followed by a structure which through significant atomic relaxation, exhibits an interesting morphological transformation into a structure with a Ce$_2$O$_3$(0001)-like surface.

[1] B. Delley, J. Chem. Phys. 92, 508 (1990); ibid. 113, 7756 (2000).

[2] K. Reuter, C. Stampfl and M. Scheffler, in Handbook of Materials Modeling, Volume 1, Fundamental Models and Methods, Sidney Yip (Ed) (2005).

2:40pm **SS2-WeA4 Revealing Atomic Structures on Oxide Surfaces with the Dynamic Force Microscope**, ***M. Reichling***, Universität Osnabrück, Germany **INVITED**

Nanostructures on oxides are most important in numerous fields of science and technology. One of the most prominent ones is chemical catalysis where oxides play a major role as support, storage material and in providing catalytically active centres. Dynamic scanning force microscopy (SFM) operated in the non-contact mode is the method of choice for the atomic scale characterisation of oxide surfaces and nanostructures on surfaces. The state of the art in highest resolution dynamic SFM on oxide systems is illustrated for structures on $CeO_2(111)$, $TiO_2(110)$, and $Al_2O_3/Ni_3Al(111)$. Individual atoms and atomic arrangements can be imaged and in some cases a quantitative understanding of atomic contrast formation can be obtained with the help of atomistic simulations. Defects are revealed to play a major role in surface chemical reactions studied at the atomic scale while the dynamic SFM also facilitates the manipulation of molecules on oxide surfaces.

4:00pm **SS2-WeA8 The Use of High-Field Nuclear Magnetic Resonance Spectroscopy to Study the Surface Structure of Poorly Crystalline γ-Al_2O_3 Surfaces**, *J.H. Kwak, J.Z. Hu, D.H. Kim, J. Szanyi,* ***C.H.F. 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 catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-Al_2O_3, 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-Al_2O_3, 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-Al_2O_3, relating its surface structure to the origin of Lewis acidity has been of considerable interest and has been studied by FTIR and solid state NMR spectroscopies, and most recently by theoretical calculations. In this presentation, we report the first use of very high field (21.1T) NMR to identify and quantify surface Al species thought to be responsible for imparting Lewis acidity to the γ-Al_2O_3 surface. In particular, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, can be assigned to 5-coordinated Al^{3+} ions, and can be clearly distinguished from the two other peaks representing Al^{3+} ions in tetra-, and octahedral coordination sites. Spin-lattice ^{27}Al relaxation time measurements clearly show that these penta-coordinated Al^{3+} sites are located on the surface of the γ-Al_2O_3 support. Furthermore, we report the first observation of preferential anchoring of an impregnated catalytic phase onto these penta-coordinated Al^{3+} sites by noting that BaO deposition onto γ-alumina resulted in the loss of intensity of the 23 ppm peak, and that the intensity loss observed was linearly proportional to the amount of BaO deposited. Thus, the results of this study strongly suggest that, at least for BaO, these penta-coordinated Al^{3+} ions are the nucleation sites. The implications of these results, especially with respect to the recent and extensive use of theoretical calculations for determining the γ-Al_2O_3 surface structure, will be discussed.

4:20pm **SS2-WeA9 Ab Initio Studies of Adsorption and Diffusion Processes on α-Al_2O_3 (0001) Surfaces**, ***E. Wallin***, *J.M. Andersson, E.P. Münger, V. Chirita, U. Helmersson*, Linköping University, Sweden

Alumina, Al_2O_3, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. Consequently, alumina thin film growth has been studied intensely in the past. However, the mechanisms behind the formation of different phases and microstructures are still poorly understood, especially for physically vapor deposited films. An increased atomic scale understanding of alumina surface processes would thus be an important step towards a more complete understanding and control of the deposition process. In the present work, density functional theory based methods were used to study the adsorption of Al, O, AlO, and O_2 on differently terminated α-alumina (0001) surfaces. The results show, e.g., that several metastable adsorption sites exist on the O-terminated surface, providing a possible explanation for the difficulties in growing α-alumina at lower temperatures, where the energy available for adatom diffusion to the bulk site might be insufficient. Moreover, the results show that Al adsorption in the bulk position is unstable or considerably weakened for completely hydrogenated surfaces, indicating that hydrogen, e.g. stemming from residual water in vacuum systems, might hinder crystalline α-alumina growth. Furthermore, energy barriers for different surface diffusion processes were investigated using the nudged elastic band method, showing, e.g., that the Al surface diffusion barrier is 0.7 eV on the Al-terminated (0001) surface. This is lower than what might be expected for a phase where synthesis at low temperatures is difficult (which is the case for α-alumina), supporting previous experimental studies suggesting the nucleation step of growth to be of crucial importance (see, e.g., Andersson et al., J. Vac. Sci. Technol. A 22, 117 (2004)). The computational results are discussed in the context of alumina growth and provide important insight into how different factors influence the growth and how deposition processes can be optimized in order to synthesize alumina films with desired properties.

4:40pm **SS2-WeA10 Iron Oxide Thin Films on Pd(111) and Pt(111)**, ***L.R. Merte***, *J. Knudsen, H.H. Sørensen, R.T. Vang,* University of Aarhus, Denmark, *M. Mavrikakis,* University of Wisconsin-Madison, *F. Besenbacher*, University of Aarhus, Denmark

The Water Gas Shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) plays an important role in the production of clean hydrogen from fossil fuels by reducing the concentration of CO in the reformed gas mixture and increasing the yield of hydrogen. The catalysts currently available necessitate a two-stage WGS process, where a high-temperature reactor is used to obtain sufficient turnover rates and a low-temperature reactor is used to push the equilibrium of the exothermic WGS reaction towards CO_2 and H_2 and thereby achieve higher overall conversion. Proposed systems for on-board hydrogen production to power, for example, vehicle-mounted fuel cells would require a WGS catalyst that is sufficiently active at low temperatures and is robust against degradation and poisoning under intermittent operating conditions. Development of such catalysts is therefore important if this technology is to be implemented. Iron-doped palladium based catalysts have been shown to be interesting candidates in this regard[1], and our goal has been to expand our current understanding of the basic processes occurring in the Fe/Pd system, among which is the formation of iron oxide under WGS conditions. In this study we have synthesized different model systems consisting of thin iron oxide films on Pd(111) and, for comparison, Pt(111) and have shown through scanning tunnelling microscopy (STM) measurements that the morphology of these films depends strongly on the preparation conditions. Furthermore, we have studied the interaction of these films with hydrogen and the structural changes occurring upon reduction. We have also used thermal desorption spectroscopy (TDS) to examine the interaction of CO with these model systems in order to identify any chemical properties unique to the Fe/Pd system that may be relevant for the WGS reaction.

[1] Zhao, S. and R. J. Gorte (2004). "The activity of Fe-Pd alloys for the water-gas shift reaction." Catalysis Letters 92(1-2): 75-80.

5:00pm **SS2-WeA11 Factors Affecting Polarization Dependent Adsorption on Ferroelectric Oxide Surfaces**, *D.B. Li, J. Garra, A. Kolpak, A. Rappe,* ***D.A. Bonnell***, University of Pennsylvania

Domain specific chemical reactivity has been demonstrated for ferroelectric surfaces in ambient and aqueous environments. To understand the factors that affect polarization dependent adsorption on ferroelectric surfaces, in situ studies in UHV were carried out on $BaTiO_3$ and lead zirconate titanate (PZT) surfaces. Polarization was oriented in situ with a metal coated scanning probe microscope (SPM) tip, surfaces were exposed to CO_2 at various dosages, and adsorption was monitored through its effect on local surface potential. Using SPM, we poled the ferroelectric substrates such that sub-micron meter sized out-of-plane domains terminate the surfaces. Surface potentials of these positive and negative domains were then measured by frequency modulation scanning surface potential microscopy (FM-SSPM). The influence of domain polarization on molecular adsorption was examined by comparing surface potential variation as a function of CO_2 dosages. Positive and negative domains exhibited quantitatively different variations in surface potential. The differences are discussed in terms of possible adsorption mechanisms. The effect of the magnitude of the polarization is examined by comparing results on PZT and $BaTiO_3$ with first principles calculations of surface relaxations and associated adsorption energies. The effect of defects is examined by comparing results on $BaTiO_3$ single crystals before and after UHV annealing to produce oxygen vacancies.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-ThM

Surface Science Challenges for Solar Energy Conversion

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:00am **EN+SS+TF-ThM1 Thermal and Photoreactions of Catechol on TiO_2**, ***P. Jacobson***, Tulane University, *X.-Q. Gong, M. Connors, A. Selloni*, Princeton University, *U. Diebold*, Tulane University

The wide band gap of titanium dioxide limits its use as a photocatalytic and photovoltaic material with solar radiation as its source. One method to increase the absorption of light at visible wavelengths is by attaching metallo-organic dye complexes. These dyes frequently use catechol and phosphonic or carboxylic acids to link the dye to the titanium dioxide surface. In an attempt to better understand the adsorption of these complex dyes, we have studied the adsorption of catechol (1,2-benzenediol) on the (110) and (011) faces of rutile titanium dioxide. Catechol was preferred over 'real' dye complexes for its ease of deposition under high vacuum conditions and simple chemical makeup. Ultraviolet photoemission spectroscopy shows a gap state introduced to the TiO_2 upon catechol adsorption. Increases in the Oxygen 1s shoulder in XPS indicate dissociative adsorption of catechol and formation of surface hydroxyls. For catechol adsorption on the rutile (110) surface a 3x1 overlayer results. Similarly, adsorption on the (011) surface forms a 2x1 overlayer. Formation of surface hydroxyls upon adsorption is believed to play a role in the formation of these ordered structures. To further study the catechol - titanium dioxide complex, temperature dependent measurements using STM, XPS, and UPS were made in the presence and absence of molecular oxygen. The difference in decomposition and intermediates formed will be discussed. These techniques were also used to study UV induced photoreactions of catechol on TiO_2.

8:20am **EN+SS+TF-ThM2 N Incorporation and Electronic Structure in High-Quality Epitaxial N-doped TiO_2 Anatase Grown by Molecular Beam Epitaxy**, ***S.H. Cheung***, *P. Nachimuthu, M.H. Engelhard*, Pacific Northwest National Laboratory, *M.K. Bowman*, The University of Alabama, *S.A. Chambers*, Pacific Northwest National Laboratory

N doping in TiO_2 is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. We have previously investigated high-quality N-doped TiO_2 rutile grown homoepitaxially by molecular beam epitaxy (MBE) on $TiO_2(110)$ and $\alpha\text{-}Al_2O_3(0001)$.[1] To gain broader understanding of N-doped TiO_2, we now report a detailed study of N incorporation and the associated electronic structure in high-quality TiO_2 anastase grown by MBE on $LaAlO_3(001)$. A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied from an effusion cell. The much higher thermodynamic stability of Ti-O bonds compared to Ti-N bonds resulted in N incorporation being limited to less than 1 at. %. The high degree of structural quality was evidenced by the observation of finite thickness fringes in the vicinity of the (004) Bragg peak in high-resolution X-ray diffraction. A formal charge of -3 on substitutional N was deduced from high-resolution XPS. Photoconductivity measurement capability is being set up at the time of abstract preparation and experimental results elucidating the role of substitutional N in reducing the bandgap will be presented at the meeting.

[1] S.H. Cheung, P. Nachimuthu, A.G. Joly, M.H. Engelhard, M.K. Bowman, S.A. Chambers, Surf. Sci. 601 (2007) 1754.

8:40am **EN+SS+TF-ThM3 Lattice Site Location for N in Homoepitaxial N-doped TiO_2 (110)**, ***V. Shutthanandan***, *S.H. Cheung, S. Thevuthasan, P. Nachimuthu, S.A. Chambers*, Pacific Northwest National Laboratory

TiO_2 is one of the most heavily studied materials for photocatalytic water splitting even though the optical absorption spectrum of TiO_2 has poor overlap with the solar spectrum, and the e^-/h^+ pair recombination rate is high. Bandgap reduction is one approach to enhancing visible light absorption. N doping causes a redshift of the bandgap into the visible and visible-light-induced photochemistry has been observed in this material. We have grown $TiO_{2-x}N_x$ rutile epitaxial films on rutile TiO_2 (110) single crystal substrates using oxygen plasma assisted molecular beam epitaxy. The N concentration (x) was varied by careful control of the atomic fluxes. The N dopant site location was studied using nuclear reaction analysis (NRA) and Rutherford backscattering spectrometry (RBS) in channeling and random geometries. $^{14}N(d,\alpha)^{12}C$ and $^{16}O(d,p)^{17}O$ nuclear reactions were used to identify the locations of N and O, respectively. NRA measurements in a channeling geometry for x = 0.04 and 0.05 clearly show that N substitutes for O in this concentration range. The x = 0.04 film shows a higher degree of N substitution (~98%) than the x = 0.05 film (~75%). Angular scans obtained around <110> for the x = 0.04 film exhibit a N angular half width that is slightly narrower (~0.05°) than that of host O. This narrowing is an indication that the N atoms are slightly displaced from the idealized anion lattice sites. The angular yield scan obtained for the x = 0.05 film exhibits a slightly larger angular half width for O, indicating that O positions are perturbed by N incorporation. In contrast, NRA and RBS measurements performed on the x = 0.12 film reveal that most of the N occupies random positions within the film, and glancing incidence XRD reveals limited Ti_2N secondary phase formation. These results clearly demonstrate that the upper limit of N solid solubility in crystalline TiO_2 rutile is ~3 at. % of the anions. Higher N concentrations can be incorporated by varying the growth conditions to facilitate defect formation, but the quality of the materials drops considerably and secondary phase formation occurs.

9:00am **EN+SS+TF-ThM4 Photochemically Activated Tethering of Molecular Monolayers to Anatase and Rutile TiO_2 Surfaces**, ***H.J. Kim***, *E.C. Landis*, University of Wisconsin-Madison, *S.H. Cheung, S.A. Chambers*, Pacific Northwest National Laboratory, *T.F. Kuech, R.J. Hamers*, University of Wisconsin-Madison

Molecular interfaces to TiO_2 are an important component of dye-sensitized solar cells and other emerging systems for solar-to-electrical and solar-to-fuel conversion. Using X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy,we demonstrate that organic alkenes will link to the surfaces of titanium dioxide in both anatase and rutile forms when illuminated with ultraviolet light. This provides a versatile way to covalently link functional organic molecules directly to oxide semiconductors. Measurements have been performed on epitaxial thin films of anatase (001), bulk crystals of anatase(101), rutile (001), rutile (110), and nanocrystalline anatase. Quantitative XPS measurements have been used to investigate the kinetics of functionalization and its dependence on the structure of the bulk samples and the dependence on exposed crystal face. We will compare the functionalization of these surfaces and discuss the mechanism of the modification. Implications for tethering of photochemically active molecules to these surfaces will be discussed.

9:20am **EN+SS+TF-ThM5 Progress and Challenges in Solar Energy Conversion Using Semiconductor/Liquid Junctions**, ***N.S. Lewis***, California Institute of Technology **INVITED**

Semiconductor/liquid contacts are useful in photoelectrochemical cells as well as for probing the fundamental surface chemistry and surface physics of semiconductors. In this talk, we will discuss the thermodynamics and dynamics of charge flow across semiconductor/liquid interfaces with an emphasis on comparison of theory and experiment for charge transfer in 1-electron outer-sphere redox systems. In addition, we will discuss the principles of surface modification to control the electrical, electronic, and chemical properties of Si surfaces. Finally, we will discuss the use of photoelectrochemistry in transport, localization, and movement of charge molecules in three dimensions in solution in real time.

10:00am **EN+SS+TF-ThM7 An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale: Towards an Optimum Morphology for Photovoltaic Devices**, ***R. Otero***, *D. Ecija*, Universidad Autonoma de Madrid, Spain, *G. Fernandez*, Universidad Complutense de Madrid, Spain, *J.M. Gallego*, ICMM-CSIC, Spain, *L. Sanchez, N. Martin*, Universidad Complutense de Madrid, Spain, *R. Miranda*, Universidad Autonoma de Madrid, Spain

One of the major factors limiting the efficiency of organic photovoltaic devices is the fact that, instead of free electron-hole pairs, photon absorption usually leads to the formation of tightly bound excitons (bound states of an electron-hole pair) which can diffuse only for a characteristic length of about 10 nm before radiative recombination occurs. The hitherto most successful approach to promote the dissociation of the photogenerated excitons is to use blends of phase-segregated electron-donor/electron-acceptor molecules; the so-called bulk heterojunction concept. At the interface between electron-donor and electron-acceptor areas, the difference in electron affinities drives the exciton dissociation by injecting free electrons (holes) into the electron-acceptor (electron-donor) areas. Provided that continuously connected paths between the interfaces and the electrodes exist, the free electrons and holes will be collected therein. From these considerations a number of morphological criteria can be extracted for optimum solar cell performance: first, the segregated electron-donor and acceptor domains must have a typical size of the order of the exciton diffusion length, in order to avoid wasteful radiative recombination events; second, the interface area between donor and acceptor domains, where exciton dissociation takes place, must be maximized; and, finally, donor (acceptor) domains must be continuously connected to the cathode (anode) to favour efficient charge transport. A morphology that would satisfy these three criteria could be a lateral superlattice of donor and acceptor areas with typical dimensions of some 10 nm. In this work we describe variable-temperature Scanning Tunneling Microscopy (STM) experiments that show how monolayer-thick blends of the electron donor molecule (exTTF) with the electron acceptor (PCBM) on a reconstructed Au(111) surface, segregates laterally into 'nanostripes' whose width is of the order of the exciton diffusion length; it thus corresponds closely with the morphology for optimum solar cell performance. The reason for such a peculiar nano-scale morphology can be traced back to the different interactions between the two molecular species and the herringbone reconstruction of Au(111). Our results demonstrate the potential of atomistic studies about the growth of organic semiconductors to open new directions for the design and construction of highly-efficient organic electronic devices.

10:20am **EN+SS+TF-ThM8 Solar Water Splitting for Renewable Hydrogen Production: The Role of N and Surface Modification in the Improved Stability of III-V Nitride Photoelectrodes**, *T. Schiros, J. Leisch, **L.-Å Näslund**, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*, T. Deutsch, J. Geisz, S. Kurtz,* National Renewable Energy Laboratory*, R. Kirby, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

III-V semiconductors are promising materials for photoelectrochemical (PEC) hydrogen production, however, material stability is a serious issue. The addition of dilute amounts of nitrogen to GaP and surface modification such as platinization result in dramatic increases in photocorrosion resistance, but the underlying mechanism is not known. We combine surface-sensitive core-level x-ray spectroscopy and microscopy with electrochemical measurements to study changes in the chemical environment and local morphology at the semiconductor-electrolyte interface during PEC hydrogen production and reveal the role of nitrogen and the platinum catalyst treatment in preserving the integrity of the surface. A detailed understanding of the interface is essential to improve control of photocorrosion and increase device stability.

10:40am **EN+SS+TF-ThM9 Surface Nanostructure and Nanochemistry of $CuInSe_2$ by Scanning Tunneling Microscopy**, *M. Mayer, L. Ruppalt, J. Lyding, **A. Rockett***, University of Illinois

Results of the characterization of the surface physical, chemical and energy band structure of $CuInSe_2$ (CIS) are reported based on scanning tunneling microscopy (STM) studies of epitaxial CIS thin films. Cu(In, Ga)Se_2 (CIGS) is the absorber layer in the highest efficiency thin-film solar cells. However, this material does not perform as well as expected, most likely due to local defects and composition fluctuations. These lead to the formation of electronic defect levels in the energy gap and band edge fluctuations, both of which can cause carrier recombination. STM images compare the structure of cleaved (110) type surfaces, which have been shown previously to be energetically unstable, with epitaxial layers of various stable surface orientations that had been cleaned by sputtering and annealing. The energetically favorable close-packed tetragonal (112) surface showed triangular facets in agreement with AFM and SEM images. The (110) face showed structural and chemical correlations with the local density of states and evidence of a Cu-deficient surface consisting of extended In-rich rows. The surface structure of the cleaved surface is consistent with suggestions that the surfaces of group III rich CIGS should be highly In-rich and should contain Cu vacancies. No significant reconstruction associated with the Se sublattice was observed. The local density of states obtained from tunneling spectroscopy exhibited large fluctuations in the energy gap and Fermi energy, providing direct evidence of the band edge fluctuations observed by photoluminescence. The gap fluctuations are correlated with the surface topography and have direct implications for the device performances.

Surface Science

Room: 608 - Session SS1-ThM

Oxide Surface Structure II

Moderator: F.P. Netzer, Karl-Franzens University Graz, Austria

8:00am **SS1-ThM1 Observation of a ($\sqrt{3}$ x $\sqrt{3}$)R30° Reconstruction on ZnO (000-1)**, ***S.T. King**, S.S. Parihar, K. Pradhan, H.T. Johnson-Steigelman,* University of Wisconsin - Milwaukee*, Z. Zhang, P. Zschack,* Argonne National Laboratory*, P.F. Lyman*, University of Wisconsin - Milwaukee

High energy polar-terminated metal oxide surfaces stabilize by a fascinating set of energy-lowering mechanisms.[1] While MgO(111) and NiO(111) stabilize via a sequence of surface reconstructions, most studies have shown that the (0001) (Zn-polar) and (000-1) (O-polar) faces of ZnO remain unreconstructed. Surface stabilization has been attributed to incomplete charge transfer between the Zn- and O-polar surfaces resulting in metallic surface states.[2] However, a recent He-atom scattering study of H-free ZnO (000-1) observed a (1x3) reconstruction, which de-reconstructs upon H exposure.[3] We extend the knowledge of ZnO surface reconstructions by investigating a ($\sqrt{3}$x$\sqrt{3}$)R30° reconstruction on ZnO (000-1) by low energy electron diffraction, x-ray photoelectron spectroscopy, and surface x-ray diffraction. While this reconstruction has been observed on the (0001) face,[4] to our knowledge this is the first reported observation on the O-polar surface. The implications of this reconstruction on understanding ZnO surface stabilization mechanisms will be discussed.

[1] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)

[2] A. Wander et al., Phys. Rev. Lett. 86, 3811 (2001)

[3] M. Kunat et al., Phys. Rev. B 66, 081402(R) (2002)

[4] Y. Margoninski and R. E. Kirby, J. Phys. C 8, 1516 (1975)

8:20am **SS1-ThM2 $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ Rocksalt Oxide Surfaces: Novel Environment for Cu^{2+}, Zn^{2+} and Its Effect on the NiO Electronic Structure**, *K.J. Gaskell, **M.A. Langell***, University of Nebraska

The effect on surface composition, electronic structure and bonding has been investigated for rocksalt $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ solid solutions, which form at the nickel-rich end of the phase diagram up to approximately x = 0.3. Octahedral coordination presents an unusual environment in solid state oxides for the "guest" Cu^{2+} and Zn^{2+} cations, and their bonding properties can be shown to be significantly different in the rocksalt environment. For example, ab initio calculations of the $Zn_xNi_{1-x}O$ valence band structure indicate that zinc interacts with the lattice oxygen primarily through the Zn 4s orbitals and is less covalent than in wurtzite ZnO. Photoemission results also provide insight into the bonding, and the Ni 2p photoemission changes substantially with increased guest ion concentration due to attenuation in non-local screening effects. The charge-transfer nature of the NiO electronic structure, however, remains largely intact. Auger parameter analysis confirms that the guest ions are octahedrally coordinated, and Auger and x-ray photoelectron spectroscopies show comparable surface and bulk concentrations until phase separation occurs.

8:40am **SS1-ThM3 Surface Study of In_2O_3 and Sn-doped In_2O_3 Thin Films with (100) and (111) Orientations**, ***E.H. Morales***, Tulane University*, M. Batzill*, University of South Florida*, U. Diebold*, Tulane University

In_2O_3 and Sn-doped In_2O_3 (Indium-Tin Oxide, ITO) exhibit optical transparency combined with low electrical resistivity, and find application in flat panel displays and solar cells. Relatively little is known about their atomic-scale surface properties, mainly because of challenges in preparing single crystal samples. We have grown epitaxial In_2O_3 and ITO films on Yttrium Stabilized Zirconia. The (100) surface has polar character, and the (111) orientation is non-polar. The films were prepared using oxygen-plasma assisted electron beam epitaxy in ultra high vacuum (UHV) conditions. The growth was monitored with Reflection High Energy Electron Diffraction (RHEED). Samples were characterized with X-ray Photoemission Spectroscopy (XPS) and Angle Resolved XPS (ARXPS) using Al-Ka radiation and Low Energy Electron Diffraction (LEED) in-situ, as well as synchrotron-based Ultra-Violet Photoemission Spectroscopy (UPS) . The films were stoichiometric, except for ITO(100), where ARXPS indicates Sn segregation. In_2O_3 (100) shows faceting in LEED, while ITO(100) stays flat with a 1x1 surface termination. Thus, it appears that Sn-segregation to the surface stabilizes the polar In_2O_3 (100). In_2O_3 (111) exhibits a ($\sqrt{3}$x$\sqrt{3}$)R30° reconstruction in LEED. Up to 9 at% Sn in ITO (111) does not seem to alter this reconstruction. Resonant photoemission measurements indicate a Sn-derived band gap state with resonance at 30 eV photon energy on the ITO (100) film; this gap state is far less pronounced on ITO (111). Interestingly, the valence band maximum is located at 2.5 and 2.7 eV below the (surface) Fermi level for ITO (100) and (111), respectively. This is ca. 1 eV higher than expected for a heavily n-type doped material with a direct optical band gap of 3.7 eV. Reasons for this apparent discrepancy will be discussed.

9:00am **SS1-ThM4 Structure of the Polar Oxide Surface MgO(111) $(\sqrt{3} \times \sqrt{3})R30^\circ$**, ***S.E. Chamberlin***, *H.C. Poon*, *D.K. Saldin*, *C.J. Hirschmugl*, University of Wisconsin - Milwaukee

Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g. a hydroxylated surface, 2.) surface faceting, and 3.) metallization.[1] MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures and reconstruct when heated to higher temperatures,[2] and thus represents an ideal system for detailed structural analysis. Detailed surface structure for the 1x1 and progress towards a structure for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction will be presented. The data have recently been obtained with a novel, low-current delay-line-detector LEED (DLD-LEED) system to minimize electron damage. An hydroxylated 1x1 surface was found to be in good agreement with photoelectron diffraction and electronic structure calculations,[3] but LEED-IV and Direct Methods results for the MgO(111) $(\sqrt{3} \times \sqrt{3})R30^\circ$ will be shown where the structure does not agree with previously published models.[2,4]

References

[1] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)

[2] R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L.D. Marks, M. Gajdardziska-Josifovska, Phys. Rev. Lett. 81, 4891 (1998)

[3] V.K. Lazarov, R. Plass, H.C. Poon, D.K. Saldin, M. Weinert, S.A. Chambers, M. Gajdardziska-Josifovska, Phys. Rev. B 71, 115434 (2005)

[4] A. Subramanian, L.D. Marks, O. Warschkow, D.E. Ellis, Phys. Rev. Lett. 92, 200411 (2004)

9:20am **SS1-ThM5 Monocrystalline TiO_2 Nanoparticles Growth on Au(111) Surface by RLAD Method**, ***D.V. Potapenko***, Columbia University, *J. Hrbek*, Brookhaven National Laboratory, *R.M. Osgood*, Columbia University

Titanium oxide is a promising photocatalytic material and has been the subject of much research throughout the last two decades. Nanostructuring is one approach for tailoring the properties of a catalyst. Recently, two methods of preparation of titania nanoparticles on Au(111) surfaces were reported (Z. Song at al. 2005 and E. Farfan-Arribas et al. 2005); yet no light-induced chemistry was observed on such nanoparticles to date. In order to prepare photoactive nanoparticles, we have conducted an extensive STM study of the growth of TiO_2 on a Au(111) surface by Reactive Layer Assisted Deposition (RLAD). The method consists of physical vapor deposition of Ti on a predeposited layer of oxygen-containing reactant followed by annealing to a higher temperature that removes the excess of the reactant. In the experiments with water as a reactive layer, we investigated the dependence of morphology of the produced arrays of titania nanoparticles on the thickness of the water multilayers. At water coverages above 50 ML we found evidence for role of an intermediate liquid water layer formed as the temperature is increased. The dynamics of water evaporation, rather than the underlying Au surface reconstruction, determined the particle distribution on the surface in this case. This relatively thick water layer also has caused us to observe evidence of the titanium hydride formation. At temperatures above 300 K the hydride decomposed leaving the titanium buried under a gold layer. The typical size of initially formed titania nanoparticles was 1 nm. At more elevated temperatures, nanoparticles coalesced so that by a temperature of 900 K about 80 % of the titania material was converted into single-crystal, flat islands with edges parallel to Au [1-10] directions, with their heights being a multiple of 0.55 nm. The atomic structure of the islands will be discussed. We have also attempted to use NH_4NO_3 as a reactive layer and the corresponding results will be presented.

9:40am **SS1-ThM6 Reactive Ballistic Deposition of Porous TiO_2 Films**, ***D.W. Flaherty***, University of Texas at Austin, *Z. Dohnálek*, Pacific Northwest National Laboratory, *T.E. Engstrom*, University of Texas at Austin, *A. Dohnálková*, *B.W. Arey*, *D.E. McCready*, *N. Ponnusamy*, Pacific Northwest National Laboratory, *C.B. Mullins*, University of Texas at Austin, *B.D. Kay*, Pacific Northwest National Laboratory

Nanoporous, high-surface area films of TiO_2 are synthesized by reactive ballistic deposition of titanium metal in an oxygen ambient.[1] Auger electron spectroscopy (AES) is used to investigate the stoichiometric dependence of the films on growth conditions (surface temperature and partial pressure of oxygen). Scanning and transmission electron microscopies show that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of N_2. TiO_2 films deposited at 50 K at 70° from substrate normal display the greatest specific surface area of 100 m^2/g. In addition, the films retain greater than 70% of their original surface area after annealing to 600 K. The combination of high surface area and thermal stability suggests that these films could serve as supports for applications in heterogeneous catalysis. The research described in this presentation 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.

[1] David W. Flaherty, Zdenek Dohnálek, Alice Dohnálková, Bruce W. Arey, David E. McCready, Nachimuthu Ponnusamy, C. Buddie Mullins, and Bruce D. Kay, J. Phys. Chem. C 111 (2007) 4765-4773.

10:00am **SS1-ThM7 Complexities and Surprises in the Epitaxial Growth of Pure and Doped TiO_2**, ***S.A. Chambers***, Pacific Northwest National Laboratory **INVITED**

TiO_2 is a transition metal oxide of considerable interest in several areas of surface, interface and thin-film science. Recent cation doping film growth studies show that certain transition metal dopants with unpaired d electrons, in concert with structural defects, impart a new form of high-temperature ferromagnetism in which dopant spins are aligned by electrons associated with the defects.[1-3] Anion (principally N) doping film growth studies show that substitutional N gives rise to a substantial red shift in the bandgap, paving the way for enhanced visible solar light absorption and the associated photophysical and photochemical energy conversion processes. However, N, which should be an acceptor in TiO_2, is actually fully compensated by conduction band electrons from interstitial Ti(III), which in turn results from Ti indiffusion during growth.[4,5] These insights were gained by our ability to grow and painstakingly characterize very well-defined, high-quality epitaxial films of pure and doped TiO_2. In the process of growing these materials with an unprecedented level of control, we have learned a great deal about the nucleation and growth of the different polymorphs of TiO_2.[6] The roles of atomic fluxes, growth temperature, dopants, overall growth rate and substrate structural properties have been elucidated one by one, and these results constitute a rich source of insight into the way transition metal oxide films nucleate and grow. In this talk, I will give an overview of our work on pure and doped rutile and anatase homoepitaxy and heteroepitaxy. This work has been supported by the US DOE, Office of Science, Division of Materials Science and Engineering, and Division of Chemical Sciences.

[1] T. C. Kaspar et al., Phys. Rev. Lett. 95, 217203 (2005).

[2] T. C. Kaspar et al., J. Vac. Sci. & Technol. B 24, 2012 (2006).

[3] T. C. Kaspar et al. Phys. Rev. B 73, 155327 (2006).

[4] S. H. Cheung et al., Surf. Sci. 601, 1754 (2007).

[5] S. A. Chambers et al., Chem. Phys., to appear (2007).

[6] R. Shao et al., Surf. Sci. 601, 1582 (2007).

10:40am **SS1-ThM9 In-Situ Polarization and Structure of 4 and 10 Layer Epitaxial $BaTiO_3$ Films**, ***A.P. Baddorf***, Oak Ridge National Laboratory, *J. Shin*, *V.B. Nascimento*, University of Tennessee, *S.V. Kalinin*, Oak Ridge National Laboratory, *E.W. Plummer*, University of Tennessee

Ultrathin films of ferroelectric materials lose their ferroelectric properties due to the depolarizing field opposing the polarization. It is important to understand the limits and conditions limiting nanoscale ferroelectrics, which are being considered for a number of sensors, memories, and transistor devices. For $BaTiO_3$, ferroelectricity has previously been observed experimentally down to 12 layers and predicted by first-principles calculations in 6 layer films. Film environment and interfaces play a critical role in ferroelectric properties. We have grown BaTiO3 ultra-thin films $SrRuO_3/SrTiO_3$ using laser-MBE in high oxygen pressures (10 mTorr). The large 2.3% lattice mismatch in this system requires careful choice of growth conditions. For ultrathin films, RHEED oscillations and patterns during growth show that layer-by-layer growth of flat, highly strained films is possible. We report in-situ, ultrahigh vacuum characterization of epitaxial films using low energy electron diffraction (LEED I-V) and scanning tunneling spectroscopy (STS). Films produce sharp (1x1) LEED patterns, indicating a well-ordered tetragonal phase structure. Comparison of observed diffraction intensities for 4 and 10 layer films at 130 and 300 K with calculated intensities reveals a vertical displacement of the central Ti, corresponding to a polarization consistent with compressive strain. Structures and polarization change dramatically after exposure to small quantities of water. STS shows discontinuous jumps at +/- 2.5 V that may indicate polarization switching. Research was sponsored by the Division of Materials Sciences and Engineering and the Center for Nanophase Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

Surface Science

Room: 611 - Session SS2-ThM

Surface Structure of Compound Semiconductors

Moderator: Y.J. Chabal, Rutgers University

8:00am **SS2-ThM1 Structural and Surface-Morphological Analysis of InN Layers Grown by HPCVD**, ***G. Durkaya***, *M. Alevli, R. Atalay,* Georgia State University, *W. Fenwick, I. Ferguson,* Georgia Institute of Technology, *N. Dietz*, Georgia State University

InN, a promising group III-nitride material for development of advanced optoelectronic structures, has still many not understood growth specific physical properties. InN layers investigated in the contribution were grown by high-pressure chemical vapor deposition (HPCVD) method, a technique that has been developed to counter the vast different partial pressures in this material system. In this study, we utilize and correlate Raman, XRD and AFM data to analyze the structural and electrical properties of the InN layers. The line shape analysis of the InN E2(high) Raman line is correlated to the crystalline quality of the layers and compared with the XRD pattern and AFM surface morphology studies for various growth conditions. The Raman line shapes for the A1(LO) phonon mode in these layers are analyzed and fitted to theoretical simulations in order to provide an estimate on the free electron concentration. The estimates are linked to results obtained by IR reflectance spectroscopy.

8:20am **SS2-ThM2 Desorption of Hydrogen from the Indium Nitride Surface Studied by HREELS**, *R.P. Bhatta,* ***B.D. Thoms***, *M. Alevli, N. Dietz*, Georgia State University

Thermal desorption of hydrogen from the N-polar InN surface has been studied by acquiring vibrational spectra using high resolution electron energy loss spectroscopy (HREELS). The reductions in intensity of the N-H stretching and bending vibrations in HREEL spectra upon annealing indicated loss of surface hydrogen and was attributed to recombinative desorption. Annealing to 375 °C for 15 min resulted in a small amount of hydrogen desorption while heating to 425 °C for the same amount of time resulted in complete removal of surface hydrogen. A shorter anneal time of 30 s raised the temperatures for both the onset and completion of desorption by about 50 °C. Since temperatures are typically 500 °C or greater for many of the common growth techniques, this result indicates that desorption of surface hydrogen is occurring during growth and may be an important mechanism for the production of reactive sites during the growth of InN. In addition to the desorption of hydrogen, an increase in the carrier concentration of the film was also observed upon annealing to 475 °C or higher as shown by a shift of the conduction band plasmon excitation to higher energy .

8:40am **SS2-ThM3 Preparation and Characterization of β-Si_3N_4 Surfaces**, ***V.M. Bermudez***, Naval Research Laboratory **INVITED**

β-Si_3N_4 is an important electronic material with numerous device applications. Yet, in contrast to other such materials, relatively little is known about its fundamental surface properties. This talk will discuss recent theoretical and experimental work relating to the preparation and properties of β-Si_3N_4 surfaces. The growth and characterization (via IR spectroscopy and XPS) of thin films will be examined, together with methods for preparing an atomically-clean and stoichiometric surface in UHV. Ab-initio calculations of the physical and electronic structure of the (0001) surface, which provide insight into the interpretation of electron-spectroscopic data, will be described. In particular the nature of the relaxation and the electronic states at the surface will be discussed. Data from Auger, photoemission (UPS and XPS) and electron energy-loss spectroscopies will be examined in relation to the theoretical results, and preliminary chemisorption data will be presented. Strong surface-charging effects are observed in UPS and XPS which take the form of rigid shifts of the spectra by 1 eV or more with adsorption and with x-ray or VUV irradiation. These will be examined in the context of electron and hole trap states in the band gap. Brief mention will also be made of IR internal-reflection studies of wet-chemical processing of β-Si_3N_4 films.

9:20am **SS2-ThM5 Linear Smoothing Coefficient in Epitaxial Growth of GaAs on Rough Substrates**, ***M.B. Whitwick***, *T. Tiedje, T. Li*, University of British Columbia, Canada

By a combination of theoretical and experimental work, using GaAs as a model system, we show that time evolution of surface morphology during epitaxial growth can be used to obtain rather detailed information on step densities and adatom dynamics. From in-situ light scattering we find that homoepitaxial growth on randomly rough GaAs (100) substrates causes the surface to smooth towards a characteristic surface roughness determined by kinetic roughening. A recent theoretical model for the surface morphology as a function of growth time,[1] based on a Burton-Cabrera-Frank picture of crystal growth[2] in which adatoms incorporate at step edges, suggests that the smoothing of GaAs can be described by a conservative Kardar-Parisi-Zhang type equation in which the dominant linear term in the growth equation is due to a negative Ehrlich-Schwoebel potential barrier for adatom migration at step edges. The surface smoothing rate is found experimentally to depend on the deposition rate and temperature during growth. In the model the coefficient of the linear term in the growth equation is inversely proportional to the step density (~F/S), where F is the flux of deposited adatoms and S is the step length density. Although the full growth equation is nonlinear, for low amplitude roughness the linear term dominates. We have used this fact to determine the linear smoothing coefficient as a function of substrate temperature (400-610 C) and growth rate (0.01-10 ML/s) by in-situ UV (244 nm) diffuse light scattering along the [011] and [01-1] directions. The coefficient of the linear smoothing term was found to have a power law dependence on flux with exponent of 0.7 and an exponential temperature dependence on temperature with activation energy 0.50 eV. The surface step density was measured ex-situ by AFM. The step density was found to be ~0.10±0.05 1/nm with a tendency towards higher density at high growth rates. This step density is in good agreement with the step density inferred from theoretical expression for the linear smoothing coefficient. The coefficient of the nonlinear smoothing term is also found to be in good agreement with theory.

[1] A. Ballestad and T. Tiedje, Phys. Rev. B 74, 153405 (2006).

[2] W.K. Burton, N. Carrera, F. Frank. Phil. Trans. Roy. Soc. 243(866):299-358. (1951).

9:40am **SS2-ThM6 Spectroscopic Study of Acid and Base-Activated Thioacetamide Passivation of GaSb and InAs Surfaces**, ***R. Stine***, U.S. Naval Research Laboratory, *D.Y. Petrovykh,* U.S. Naval Research Laboratory and University of Maryland, *E.H. Aifer, L.J. Whitman*, U.S. Naval Research Laboratory

A wide range of III-V semiconductor heterostructure devices are under development for applications in electronics, optoelectronics, and sensing. However, the performance of III-V devices following processing is often detrimentally affected by the formation of mid-bandgap electronic states and the subsequent pinning of the surface Fermi level. Chemical passivation of the device surfaces can stabilize their properties by inhibiting the regrowth of native oxides that can otherwise contribute to Fermi level pinning. Traditionally, this passivation has been accomplished by the formation of surface sulfide groups through wet chemical treatment with an inorganic sulfur-containing compound, such as ammonium sulfide or sodium sulfide. More recently, though, the use of thioacetamide (TAM), an organic sulfur containing compound, has been shown to have a number of advantages over traditional inorganic methods,[1-3] including milder reaction conditions and a higher degree of control over the reaction. Although studies have shown the effect of TAM passivation on the electronic properties of devices, little information has been available on the actual chemical reactions that take place at the surfaces. Here, we present detailed X-ray photoelectron spectroscopy (XPS) studies of these surface reactions on gallium antimonide and indium arsenide-important materials for infrared optoelectronics. A comparison of TAM passivation performed under acidic versus basic conditions shows that acidic-TAM treatment produces a thicker sulfide layer that is better suited to the prevention of re-oxidation than that formed under basic-TAM treatment, regardless of exposure time or TAM concentration. We have determined the relative amounts of III-sulfides versus V-sulfides and tracked the rate of re-oxidation for each component independently over time.

[1] Petrovykh, et al., Appl. Phys. Lett. 86, 242105 (2005)

[2] Petrovykh, et al., Surf. Interface Anal. 37, 989 (2005)

[3] Aifer, et al., Proc. SPIE 6542, in press.

10:00am **SS2-ThM7 STM Imaging and DFT Modeling of the Group III-rich Reconstruction of InAs(100)-c(8×2)/(4×2)**, ***D.L. Winn***, *J. Shen, J.B. Clemens, A.C. Kummel*, University of California, San Diego

The atomic group V reconstruction of the III-V (001) surfaces have been extensively studied since these surfaces are favorable for MBE growth. The group III rich surfaces are of III-V semiconductor can be readily prepared by heating the group V rich reconstructions. The group III rich surfaces may be favorable for ALD oxides growth since they exhibit a low reactivity to O_2 because the usually lack group V dimers. InAs(001) is well documented to have a (4×2) reconstruction, however, the details of the reconstruction are still under debate. Atomically resolved filled and empty state scanning tunneling microscopy (STM) images of the InAs(001)-c(8×2)/(4×2) surface reveal that the reconstruction is made up of single atom rows that run in the [110] direction which are separated by ~17 Å. In addition, atomically resolved STM images show that the row structure is most likely comprised of undimerized atoms. Cl2 was deposited onto the surface (which has been shown to preferentially react with III atoms on III-V semiconductors) to confirm that the rows were in fact comprised of In atoms. The experimental results suggest that the most probable structure for InAs(001)-c(8×2)/(4×2) is the undimerized or dimerized β3(4×2) reconstruction. The reconstruction consistent of a top layer of bicoordinated or tricoordinated In atoms at the center of the rows and tricoordinated As atoms in the second layer at the edges of the rows. Density functional theory (DFT) STM simulations were used to confirm the experimental findings. DFT reveals that the dimerized and undimerized structures are nearly degenerate consistent with STM images show the In dimerization may be temperature dependent. Both the undimerized and dimerized β3(4×2) structures lack As dimers and have a low reactivity to O2 consistent with a surface which is suitable for ALD gate oxide deposition.

10:20am **SS2-ThM8 Scanning Tunneling Microscopy Study of Interfacial Bonding Structure and Annealing Effect of In_2O/InAs(001)-c(8x2)/(4x2)**, ***J. Shen**, D.L. Winn, A.C. Kummel*, University of California, San Diego

The key to fabricating a III-V MOSFET is forming an electrically passive oxide-semiconductor interface. In an effort to identify an unpinned oxide/semiconductor interface on InAs, a detailed study of In_2O adsorbed to InAs(001)-c(8x2)/(4x2) was performed. Scanning tunneling microscopy (STM) and density functional theory (DFT) were used to ascertaining how In_2O adsorbates bond to the clean InAs(001)-c(8x2)/(4x2) surface. The InAs(001)-c(8x2)/(4x2) surface consists of a top row of In atoms which are bonded to tricoordinated As atoms containing partially filled dangling bonds. STM results showed that the initial In_2O molecules only occupy specific sites at the edge of the rows. These In_2O atoms most likely form new In-As bonds to the surface. This is a favorable bonding structure for oxide/semiconductor interfaces since it avoids As-O bond formation which is likely to create states in the band gap. In addition, the formation of In-As bonds restores the tricoordinated As atoms to a more bulk-like bonding environment. A height analysis was performed to determine growth mechanism. At low coverage (20% monolayer), the In_2O adsorbates formed islands that are elongated in the [110] direction. Prior to all the first layer sites being occupied with In_2O molecules, second layer growth was observed on the islands. Each layer of oxide has a distinct height, however, the second and subsequent layers appear to be amorphous. In addition, the effect of annealing In_2O/InAs(001)-c(8x2)/(4x2) was studied. The annealed samples were more ordered and uniform. The oxide molecules on the annealed samples filled in the troughs and formed ordered islands with rows in [i10] direction. Comparisons of oxide height distributions before and after annealing, show the oxide height is reduced from 1.5 Å to 1 Å. This is consistent with the In-In bond formation between two nearest neighbor In_2O atoms in the [i10] direction. Most importantly, for both room temperature deposition and annealing, the clean surfaces lattice is left unperturbed, the In_2O adsorbates never cause the abstraction of any surface atoms on the InAs(001)-c(8x2)/(4x2) surface and the In_2O molecules only occupied specific sites. The formation of an ordered oxide-interface without disruption of the InAs(100)-c(8x2)/(4x2) lattice is favorable for creating an unpinned oxide-semiconductor interface.

10:40am **SS2-ThM9 Bonding Hybridization in the Group III-rich Reconstructions of InGaAs(100)-(4×2)**, ***T. Song**, D.L. Winn, J. Shen, A.C. Kummel*, University of California, San Diego

The group-V (As or Sb) rich reconstructions of III-V semiconductors have been extensively investigated since these surfaces are favorable for MBE growth. However, the group-III (Ga or In) rich reconstructions can readily be prepared by heating the group-V rich reconstructions, and the group-III rich reconstructions may be favorable for ALD gate oxide deposition due to their low reactivity to oxygen. Although the group-III rich surfaces have several potential applications, many III-V semiconductors, including InGaAs, have unidentified group-III rich reconstructions. Four different group-III rich 4x2 reconstructions of In0.5Ga0.5As(001)-(4×2) were modeled using DFT: ζ (4×2), β2(4×2), β3(4×2), and the undimerized β3(4×2) structures. Multiple polymorphs (Ga and In positions) were investigated. The undimerized β3(4×2) reconstruction most closely matches the experimental room temperature STM images of In0.53Ga0.47As/InP(001)-c(8×2)/(4×2). This reconstruction consists of a top row of undimerized In/Ga atoms which are bonded to tri-coordinated As atoms. In the undimerized β3(4×2) structure, the row In/Ga atoms are sp hybridized. Conversely, in the dimerized β3(4×2) reconstruction, the top row In/Ga atoms are sp2 hybridized. DFT calculations showed that the undimerized β3(4×2) reconstructions are more stable in energy. The density of states (DOS) of the β3(4×2) reconstructions showed that the undimerized β3(4×2) structure had a band gap while the dimerized β3(4×2) structure was metallic. The correlation between hybridization and electronic structure is due to the influence of hybridation and bonding structure on the filling of the dangling bonds.

Surface Science

Room: 608 - Session SS1-ThA

Environmental Surfaces

Moderator: J.T. Dickinson, Washington State University

2:00pm **SS1-ThA1 Influence of Surface Oxides on the Colloidal Stability, Mobility and Sorption Properties of Carbon Nanotubes in Aquatic Environments**, ***H. Fairbrother***, *B. Smith, H.-H. Cho, F.K. Bangash, M. Shin, W.P. Ball*, Johns Hopkins University **INVITED**

Carbon nanotubes (CNTs) are a unique and versatile class of nanomaterials with enormous commercial potential. This has been responsible for a rapid increase in their production rates and, as a result, larger quantities of CNTs will inevitably find their way into the environment. The ecological and toxicological impacts of these nanomaterials are, however, still poorly understood. Many purification and functionalization strategies incorporate oxygen-containing functional groups into the surface of CNTs, and similar modifications can occur after CNTs are released into the environment through exposure to oxidizing agents. To address this issue surface analytical techniques have been developed to quantify both the concentration of oxygen and distribution of surface oxides produced on CNTs by different oxidative treatments. In this presentation the effect of oxidation and the introduction of surface oxides on the colloidal stability and sorption properties of CNTs in aquatic environments will also be discussed. A suite of CNTs with different levels of oxygen content were prepared by refluxing pristine CNTs in HNO_3 solutions of various concentrations; X-ray photoelectron spectroscopy (XPS) showed that the surface oxide concentration increased from 3% for the pristine nanomaterials to 12.5% for CNTs treated in ~16M HNO_3. The corresponding variation in oxide distribution has been probed using chemical derivatization in conjunction with XPS. UV-vis spectroscopy shows that well-defined relationships exist between the level of CNT surface oxidation and their colloidal stability; specifically, more highly oxidized CNTs remain stable over a wider range of aquatic conditions. The sorption properties of CNTs also display systematic variations as the level of surface oxidation increases: adsorption of ^{14}C labeled-naphthalene, a hydrophobic organic chemical, decreased linearly while divalent heavy metal contaminants like Zn^{2+} showed an increasing affinity towards more highly oxidized CNTs. Relationships that exist between specific types of surface oxides, particularly carboxylic acid groups, and CNT behavior in aquatic environments will also be discussed. In general, our studies highlight the fact that even comparatively small changes in surface oxygen concentration are responsible for pronounced changes in CNT properties.

2:40pm **SS1-ThA3 Reactions of Sulfur Dioxide on Calcium Carbonate and Iron Oxide Single Crystal and Particles Surfaces under Ambient Conditions**, *J. Baltrusaitis*, ***V.H. Grassian***, University of Iowa

Reactions of sulfur dioxide under ambient conditions on environmentally important interfaces - calcium carbonate and iron oxide - single crystal and particle surfaces - have been investigated. A custom-designed X-ray Photoelectron Spectroscopy (XPS) ultra-high vacuum chamber is coupled to an environmental reaction chamber so that the effects of adsorbed water and molecular oxygen on the reaction chemistry can be followed. Atomic force microscopy provides additional spatial details about the reaction chemistry. It is determined that both the extent of reaction, the chemical speciation, which includes adsorbed sulfite and adsorbed sulfate, and reaction mechanisms are controlled by the environmental conditions. In addition, the two interfaces behave quite differently. Adsorbed water plays a key role in reactions of sulfur dioxide on calcium carbonate but not on iron oxide whereas molecular oxygen enhances the extent of reaction of sulfur dioxide on iron oxide but not calcium carbonate. Mechanisms to explain the reaction chemistry of sulfur dioxide on these two important environmental interfaces under different conditions are proposed. Atmospheric and environmental implications of these reactions are also discussed.

3:00pm **SS1-ThA4 pH Dependent X-ray Photoemission Studies of Hexylamine at the Aqueous-Vapor Interface**, ***M.A. Brown***, University of California, Irvine, *B. Winter,* Max-Born-Institut fur Nichtlineare Optik und Kurzzeitspektroskopie, Germany, *M. Faubel,* Max-Planck-Institut fur Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

The understanding of molecular arrangements and interactions at the aqueous-vapor interface is important in many chemical and biological systems where the pH dependent chemistry may vary greatly from that of the bulk. We examine the surfactant properties of hexylamine (C6H13NH2) and the protonated hexylamine ion (C6H13NH3+) at the aqueous-vapor interface. The state of this acid/base equilibrium couple should shed light on the local pH of the aqueous interface, as well as the relative aqueous solvation of the two species. Chemical shifts are observed in the N (1s) and C (1s) photoemission spectra due to protonation of the amine, allowing us to clearly identify and quantify the two species. The experiments use a 15 μm liquid micro-jet free vacuum surface at a micro-focus x-ray beamline of the BESSY synchrotron radiation facility. The bulk pH of solution is varied by addition of HCl in order to vary the degree of hexylamine protonation. Varying the energy of the ejected photoelectrons by carrying out experiments as a function of x-ray wavelength allows us to generate a depth profile of the aqueous-vapor interface. The core level O (1s), N (1s) and C (1s) photoemission spectra were collected as a function of photoelectron kinetic energy, creating a molecular level picture of the entire interfacial region. Results show that the concentration of hexylamine (C6H13NH2) is greatly enhanced at the interface relative to the protonated hexylamine ion (C6H13NH3+). Peak broadening, and relative peak intensities vary with bulk pH, and are attributed to changes in molecular packing.

3:40pm **SS1-ThA6 Heterogeneous Uptake of Ozone on Solid Potassium Iodide**, *M.A. Brown, J.T. Newberg, M.J. Krisch,* University of California, Irvine, *B.S. Mun,* Advanced Light Source, LBNL, *P. Ashby,* Molecular Foundry, LBNL, ***J.C. Hemminger***, University of California, Irvine

Ozone, a powerful oxidant trace gas found throughout both the troposphere and stratosphere is believed to oxidize alkali halides in the form of sea-salt aerosols and is considered to be a significant candidate for the formation of reactive gas phase molecular halogens. Recent studies suggest that although iodide is a minor component of sea-salt spray its concentration at the interface of aqueous solutions and at the interface of dried solid crystalline sea-salt particles is greatly enhanced relative to the bulk concentration. X-ray photoelectron studies described here show, under conditions in which a low defect density KI surface is completely devoid of adsorbed water molecules the surface oxidation by ozone results in a thin molecular layer of KIO3 that is self-passivating. We report for the first time the reaction probability (?) at room temperature for the reaction KI(s) + O3(g) ? KIO3(s) of ? = 1.4 (±0.7) x 10-4. Results of the low defect density system are compared with the results of a high defect density polycrystalline KI surface. In-situ SPFM imaging provides molecular insight into the site specificity of the chemical reaction on the surface of KI (100).

4:00pm **SS1-ThA7 Surface Science Investigations of Photoprocesses in Model Interstellar Ices**, *J.D. Thrower,* Heriot-Watt Univ., UK, *D.J. Burke,* Univ. College London, UK, *M.P. Collings,* Heriot-Watt Univ., UK, *A. Dawes, P.J. Holtom,* The Open Univ., UK, *F. Jamme,* Univ. of Nottingham, UK, *P. Kendall,* The Open Univ., UK, *W.A. Brown,* Univ. College London, UK, *I.P. Clark,* Central Laser Facility, CCLRC, UK, *H.J. Fraser,* Strathclyde Univ., UK, ***M.R.S. McCoustra***, Heriot-Watt Univ., UK, *N.J. Mason,* The Open Univ., UK, *A.W. Parker*, Central Laser Facility, CCLRC, UK

In the last decade or so, the astronomy and astrophysics communities have come to realise that physical and chemical processes occurring at the surfaces of interstellar dust grains play a key role in the chemical evolution of the Universe. Grain surfaces promote the formation of molecular hydrogen and simple hydride species such as water, ammonia and methane. As such, at the temperatures found in the most chemically rich regions of the interstellar medium (ISM), typically 20 K or less, they reactively accrete icy mantles containing these species. Condensation of molecules from the gaseous ISM occurs in parallel, producing water-rich icy mantles that are readily observed in the infrared in many lines of sight towards star-forming regions. These mantles play a crucial role as reservoirs for small molecular coolants during the earliest phases of star formation, promoting the formation of small, long-lived stars such as our own Sun. They also act as chemical nanofactories driven by energy from photons and cosmic rays to produce increasingly complex chemical species from simple ice mixtures, hence seeding the Universe with a complex chemical soup. While numerous studies exist in the literature seeking to understand the chemical evolution of water-rich icy mixtures during irradiation by light and charged particles, the majority of these high vacuum studies have failed to address the fundamental question of the disposition of the incident energy. How much of the photon or charged particle's energy goes into driving physical processes (morphological change, desorption, etc.) as opposed to driving chemical processes? Here we will report on recent surface science investigations aimed at addressing this most fundamental of questions in laboratory astrochemistry.

4:20pm **SS1-ThA8 Monolayer Etch Pits Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces in 10^{-5} Pa Water Vapor**[1], ***S.C. Langford**, K. Kimura, J.T. Dickinson*, Washington State University

On single crystal NaCl, 248-nm laser radiation can roughen steps and produce monolayer islands and etch pits at fluences well below the macroscopic damage threshold.[2] These effects are dramatically altered by the presence of 10^{-5} Pa water vapor. In this work, we extend these observations to single crystal KCl and KBr. Atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in ultrahigh vacuum show monolayer islands; the island density increases with increasing laser fluence. We attribute island formation to the aggregation of alkali halide monomers desorbed from steps onto terrace sites as a consequence of UV exposure; this desorption accounts for the observed step roughening. In the presence of water vapor at pressures of 10^{-5} to 10^{-3} Pa, fifty 248-nm pulses at 100 mJ/cm^2 produce monolayer etch pits on KCl and KBr. Higher fluences are required for NaCl. Quadrupole mass spectrometry on the products emitted during laser irradiation show much more intense alkali and halogen emissions in the presence of water vapor, consistent with the observed etching. Although the mechanism for enhanced etching in the presence of water vapor is not clear, the erosion of alkali halides during electron irradiation at room temperature is hindered by the accumulation of alkali metal.[3] Water vapor may hinder alkali aggregation, perhaps by dissociative adsorption at halogen vacancies. We show that water vapor at similar partial pressures has comparable effects on alkali halide surfaces exposed to 2 keV electrons.

[1] This work was supported by the U.S. Department of Energy-under Grant DE-FG02-04ER-15618.

[2] K.H. Nwe, S.C. Langford, and J.T. Dickinson, J. Appl. Phys. 97, 043502 (2005).

[3] B.M. Szymonski, J. Ruthowski, A. Poradzisz, Z. Postawa, and B. Jørgensen, in Desorption Induced by Electronic Transitions—DIET II (Springer, Berlin, 1985), p. 160-168.

4:40pm **SS1-ThA9 The Adsorption and Desorption of H_2O, H_2S and SO_2 on Amorphous Carbon Films**, ***E. Broitman**, W. Michalak, J.B. Miller, A.J. Gellman,* Carnegie Mellon University*, M.A. Alvin,* U.S. Department of Energy

There is a renewed interest in the development of efficient catalyst-sorbents for the capture and conversion of sulfur containing compounds that poison the catalysts and separation membranes, often used in modern processes for hydrogen generation. It is well known that sulfur-containing molecules interact with activated carbon surfaces by both physisorption and chemisorption, where surface chemistry and pore structure appear to contribute to the strength of the interaction. However, because it is difficult to control and characterize their surface properties, the fundamental nature of the adsorption onto activated carbons is still not well understood. In this work, we obtain precise control of surface properties by modeling activated carbons with amorphous carbon (a-C) films deposited under ultra high vacuum conditions. Carbon films with controlled and defined microstructure (sp^2/sp^3 ratio), surface chemistry (dangling bonds, oxidation state), and morphology (roughness, porosity) were deposited by DC magnetron sputtering. Temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) were used to study H_2O, H_2S and SO_2 surface chemistry on these films. For comparison, experiments were also carried out on a highly oriented pyrolytic graphite (HOPG) surface. H_2O, H_2S and SO_2 physisorb on HOPG and on a-C films by a cluster growth mechanism. At lower coverages, the molecules adsorbed in the first two-dimensional layer and on the edges of the three dimensional (3D) islands have a weaker interaction (lower binding energy) than molecules within 3D islands. Water desorbs from a-C with one peak, while H_2S and SO_2 desorb with two features, corresponding desorption from the monolayer and the multilayer. The three adsorbates interact with the a-C surface with different strengths: at low coverage, energies of desorption, E_{des}, from a-C films were 11.3, 8.2 and 10.2 kcal/mol for H_2O, H_2S and SO_2, respectively. XPS analysis after TPD experiments on HOPG and a-C films revealed no reactions between the carbon surfaces and the adsorbates. On the other hand, H_2S adsorption on oxidized films, a-CO_x, revealed the presence of residual elemental sulfur, thereby indicating that the oxygen of the films had reacted with the adsorbate.

5:00pm **SS1-ThA10 Atomic Scale Features on Air Exposed Mica Surfaces Revealed By UHV Dynamic SFM*, F. Ostendorf*,** *C. Schmitz, S. Hirth, M. Reichling*, University of Osnabrueck, Germany

Mineral surfaces play a key role in many reactions regarding mineral dissolution, precipitation and crystal growth. The most prominent of this type of surfaces in nano biology and material science is Muscovite mica. Air cleaved mica surfaces have been investigated by dynamic force microscopy operated in the non-contact mode (NC-AFM) under ultra-high vacuum (UHV) conditions with atomic resolution. In contrast to the common assumption that a simple degas under UHV conditions leads to a true atomically flat and clean surface, we demonstrate that the sample surface always exhibits a high density of small defects and clusters. In addition to these defective features we find flat and layered, hexagonally shaped islands exhibiting two different types of atomic scale patterns on different length scales: namely a rectangular pattern and a Moiré superstructure. In general one can consider that potassium ions of a mica surface - when cleaved in air - react with water and carbon dioxide. This composes potassium carbonate. By detailed measurements with atomic precision we clearly identify the unit cells of both patterns. The rectangular pattern is associated with the potassium carbonate unit cell. For growing potassium carbonate crystallites on mica surfaces the slight lattice mismatch needs to be compensated. This compensation is reflected by the observed Moiré superstructure. Finally we yield strong evidences that crystallites of potassium carbonate emerge due to the reaction with water and carbon dioxide and grow by Ostwald ripening on mica surfaces.

Surface Science

Room: 611 - Session SS2+EM+TF-ThA

Organics and Carbon Films on Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2+EM+TF-ThA1 Reactivity of n-type/p-type H:Si(111) for Photoadsorption of CH_3Br**, ***T. Yamada***, RIKEN, Japan*, H. Ozawa,* The University of Tokyo, Japan*, H.S. Kato,* RIKEN, Japan*, M. Kawai*, RIKEN and University of Tokyo, Japan

Ultraviolet photo-assisted adsorption of CH_3Br gas was examined on hydrogen terminated Si(111)-(1x1) surfaces of n-type (P-doped, resistivity 7-10 Ωcm) and p-type (B-doped, 10-40 Ωcm) substrates. After treatment of Si substrates at $1x10^{-5}$ Pa of CH_3Br pressure with simultaneous irradiation by high-pressure Hg lamp (100W) for 10 min - 3 hours at room temperature, high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) were applied to detect the adsorbate. On n-type H:Si(111), hydrocarbon adsorbates were observed, and on p-type H:Si(111), Si-Br stretching signal (450 cm^{-1}) was exclusively detected. To survay the mechanism of reaction, we divided this adsorption process into UV irradiation in ultrahigh vacuum (UHV) and following CH_3Br introduction without UV. Although a small amount of hydrocarbon contaminant was deposited on both n-type and p-type substrates during UHV UV irradiation, the post-adsorption of CH_3Br resulted in increase of only hydrocarbons on n-type, and only Br on p-type. This result indicates that the irradiation of UV on H:Si(111) promoted photo-assisted desorption of H and leaves hydrogen vacancies, namely, dangling bonds. The difference of adsorption product between the n-type and p-type should be associated with the electronic structure of substrate modified with dopant atoms. We performed molecular-orbital calculations of various H-terminated Si(111) model clusters (sized from 32 Si atoms to 400 Si atoms) with H vacancies on the surface and a few Si atoms replaced with P or B atoms, on the basis of density functional theory (DFT). It was demonstrated that the orbital protruding over the dangling bond was the highest filled electronic orbital on P-doped cluster, whereas on B-doped, it was the lowest unoccupied orbital. This result did not change if we change the number of dangling bonds or dopant atoms. Although this approximation is too rough because of orders-of-magnitude higher dopant level than the real substrates, the result matches the classical formalism of semiconductor band bending near the surface. We further performed DFT calculations on the dangling bond coordinated with a CH_3Br molecule. The dangling bond on n-type/p-type substrate attracts theCH_3 group/Br atom, respectively. It was recognized that the effects of dopant are crucial for the adsorption selectivity of surface dangling bonds towards organic molecules.

2:20pm **SS2+EM+TF-ThA2 Effects of Dative Bond Formation on Si(114) Reaction Pathways**, ***D.E. Barlow***, Nova Research, Inc., *S.C. Erwin, A.R. Laracuente, L.J. Whitman, J.N. Russell, Jr.*, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface with a single domain-like surface reconstruction composed of parallel rows of dimers, rebonded atoms, and tetramers.[1] We have used transmission FTIR, STM, and DFT to compare the reactions of ethylene and acrylonitrile at the Si(114)-(2x1) tetramer sites. These sites have a diene-like structure, allowing us to investigate the potential Diels-Alder reactivity of an unusual Si surface structure.[2] In particular, we have investigated the effects of conjugated, electron-withdrawing substituents on the dieneophile. For organic reactions, such substituents typically increase the reaction rate, often by several orders of magnitude. Ethylene reacts as the dieneophile in a Diels-Alder reaction at the tetramer site with a reaction probability of $\sim 10^{-2}$. Surprisingly, however, we find that acrylonitrile does not undergo the Diels-Alder reaction at the tetramer sites. Rather, exposure of the clean Si(114) surface to acrylonitrile leads to three distinguishable ketenimine (-C=C=N-) structures in the FTIR spectra. Polarized transmission FTIR results indicate the presence of ordered ketenimine arrays, with strong registry to the Si(114) surface and site-dependent orientation. We have distinguished the acrylonitrile adsorption structures at the tetramer sites from those at the dimer and rebonded atom sites by analyzing site-dependent heterofunctionalized Si(114) surfaces on which we have first passivated a large portion of rebonded atom and dimer sites with ethylene, allowing the acrylonitrile to preferentially react with the remaining tetramer sites. From the polarized FTIR spectra, we conclude that the -C=C=N- structures are aligned parallel to <110> at the rebonded atom and dimer sites, but perpendicular to <110> at the tetramer sites. The differing ethylene and acrylonitrile reactivities on Si(114) further emphasize the variable reaction pathways possible for dative bonding on reconstructed Si surfaces.

[1] S. C. Erwin, A. A. Baski, and L. J. Whitman, Phys. Rev. Lett. 77, 687 (1996).

[2] D. E. Barlow, et al., J. Phys. Chem. B 110, 6841 (2006).

2:40pm **SS2+EM+TF-ThA3 Surface Chemistry of Silicon: Making the Connection to Molecules**, ***J.M. Buriak***, *D. Wang, Y. Qiao, J. Chai*, University of Alberta, Canada **INVITED**

The chemistry of semiconducting surfaces is a field of intense interest, not only for the prospect of exciting cutting edge applications, but also from a fundamental perspective.[1] Control over the surface reactivity of silicon and other semiconducting materials is critical for interfacing new molecular devices on chips and other nanotechnological applications, and to perhaps replace oxide overlayers as feature sizes on transistors become smaller than 50 nm. In this talk, we will attempt to provide a preliminary reactivity 'road map' towards understanding the organometallic surface chemistry of silicon that, interestingly, can vary greatly from that of silicon-based molecules. For example, by using the silicon surface as an electrode, electrochemistry can drive reactions that have no obvious parallels with molecular chemistry. As a result, molecules as diverse as alkynes and tetraalkylammonium salts can serve as organic sources to prepare organic monolayers directly on silicon, bound through Si-C bonds.[2] We will also discuss our latest results concerning the patterning of silicon surface reactivity on the nanoscale (features sizes<30 nm); both conjugated organic monolayers and monodisperse metallic nanocrystallites can be interfaced directly to the surface of silicon for a variety of applications.

[1] Buriak, J. M. "Organometallic Chemistry on Silicon and Germanium Surfaces", Chemical Reviews, 2002, 102, 1271-1308.

[2] Wang, D.; Buriak, J. M. "Trapping Silicon Surface-Based Radicals", Langmuir, 2006, 22 6214-6221.

3:40pm **SS2+EM+TF-ThA6 Liquid Methanol Reaction with H-terminated Silicon Surfaces**, *D.J. Michalak*, University of California, Berkeley, *S. Rivillon Amy*, Air Products and Chemicals, Inc., *A. Esteve*, LAAS, France, ***Y.J. Chabal***, Rutgers University

The reaction of hydrogen-terminated Si(111) and oxide terminated silicon surface with neat anhydrous liquid methanol (CH_3OH) has been studied with high resolution Fourier transform infrared spectroscopy (FTIR) to determine several factors regarding the surface chemistry. First, a high temperature reaction of atomically smooth H-Si(111) surfaces in neat anhydrous CH_3OH liquid produces methoxylated surfaces that are virtually free of subsurface oxidation. At long reaction times (t > 3h), the surface saturates with Si-OCH_3 sites covering ~30% of a monolayer, with a residual ~70% comprised of Si-H sites. The virtually-oxide free surface facilitates two important conclusions. First, surface reaction mechanisms involving the insertion of oxygen atoms in the subsurface Si-Si back bonds can be ruled out. Because subsurface oxidation often presents deleterious surface electrical trap states, the absence of significant oxidation also holds important implications for the use of alcohol-terminated precursors in the functionalization of surface chemistry for use in electronics devices. Second, the vibration modes of the clean surface are very sharp and allow a more careful analysis of surfaces that contain subsurface oxidation. Specifically, it has been observed previously that, despite the presence of subsurface oxidation on some methoxyl-terminated surfaces, no evidence for subsurface oxygen atoms has been observed directly below Si-H sites. This is surprising from the standpoint that the surface still retains nearly 60-70% unoxidized Si-H sites. It was proposed that the oxidation may reside underneath Si-OCH_3 sites. In this work, comparison of partially oxidized surfaces with the virtually oxide-free surfaces demonstrates that the presence of blue shifted Si-OCH_3 vibrational modes is correlated with the presence of subsurface oxidation. This assignment is corroborated by studies performed on oxide-terminated surfaces that present similar, but blue shifted modes to those observed on the oxide-free H-Si(111) surface. Thus, this work demonstrates that while virtually oxide-free surface can be made, there is a large selectivity towards the formation of oxide underneath atop Si-OCH_3 sites relative to the Si-H sites, which retain almost exclusively unoxidized backbonds. Finally, mechanisms for the formation of oxide are presented with regard to these new results.

4:00pm **SS2+EM+TF-ThA7 Dissociative Electron Attachment Induced Growth of Thin Graphite Films or Graphene on Si(111)-7×7**, ***D. Oh***, *H. Abernathy, N. Sharma, P.N. First, M. Liu, T.M. Orlando*, Georgia Institute of Technology

There is currently keen interest in developing good strategies for the growth of a few layers of graphite or graphene on substrates such as Si. We are exploring the use of low-energy electron induced dissociation of adsorbed benzene, naphthalene and phenylacetylene in the production of graphite/graphene films with good lateral heterogeneity. In this study, benzene, naphthalene or phenylacetylene is chemisorbed onto reconstructed Si(111)-7×7 surfaces. These adsorbates are fragmented via low-energy electron bombardment at energies which are dominated by dissociative electron attachment resonances. In general, the incident electron beam can be captured by low-lying π^* states of the chemical precursors and can lead to controlled dissociation and the formation of reactive radicals and negative ions. These fragments can then react to form a network structure of predominantly sp^2 hybridization. The deposited carbon overlayer is examined with Auger electron spectroscopy, Raman spectroscopy and scanning tunneling microscopy. The quality of the deposit and the viability of this non-thermal growth strategy will be discussed.

4:20pm **SS2+EM+TF-ThA8 Adsorption Irregularities of 1,3 Cyclohexadiene and Naphthalene on Silicon(100) Investigated by STM, DFT and an Extended Frontier Orbital Analysis**, ***P.M. Ryan***, CRANN, Trinity College Dublin, Ireland, *L.C. Teague*, National Institute of Standards and Technology, *J.J. Boland*, CRANN, Trinity College Dublin, Ireland

We consider the reactions of 1,3-cyclohexadiene (1,3-CHD)[1,2] and Naphthalene on Si(100) and examine possible origins for the surface adsorption selectivity evident from STM measurements. The major adsorption products for both molecules are identified by STM. DFT calculations are carried out in order to examine the energetics of the major products and their associated structural analogs. The calculations reveal that the theoretical product distributions based on thermodynamics alone, for both systems, differ significantly from the experimental ones. We explain, using an extended frontier orbital analysis, that secondary orbital interactions which can discriminate between certain concerted reactions and are unavailable at the Γ point due to symmetry considerations become feasible at other κ points in the surface Brillouin zone. We propose that these interactions play a role in the kinetics of the adsorption process and may account for the observed reaction selectivity.

[1] Teague, L.C. and J.J. Boland, STM Study of Multiple Bonding Configurations and Mechanism of 1,3-Cyclohexadiene Attachment on Si(100). Journal of Physical Chemistry B, 2003. 107(16): p. 3820-3823.

[2] Teague, L.C., D. Chen, and J.J. Boland, DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100)Surface. Journal of Physical Chemistry B, 2004. 108(23): p. 7827-7830.

4:40pm **SS2+EM+TF-ThA9 CNTs on a Si(100) Surface: Dry Deposition, STM/STS, and Contacts**, ***B. Naydenov***, Trinity College Dublin, Ireland, *J.J. Boland*, Trinity College Dublin and CRANN, Ireland

We present a cryogenic STM study of carbon nanotubes (CNTs) deposited on Si(100) surfaces. Imaging and spectroscopic results by means of LT-STM will be demonstrated and analyzed. Using STM-manipulations, contacts (different metals) with the CNTs are formed and characterized. Aspects of the CNTs purity, preparation, and interaction with the substrate will be discussed.

Surface Science

Room: 4C - Session SS-ThP

Surface Science Poster Session

SS-ThP1 Amplified Optical Switching of Surface Wettability through Tailored Morphologies, ***D. Yang***, *P. Aella, A. Garcia, D. Gust, M.A. Hayes,* Arizona State University*, S.T. Picraux*, Los Alamos National Laboratory

We report the tailoring of surface roughness to significantly amplify light-induced contact angle switching and wettability of surfaces functionalized with the photochromic azobenzene molecules. Potential applications of controlled surface wettability for microfluidic systems include delivering analyses in lab-on-a-chip environments, bio-assay in drug discovery, and chemical analyses. Transporting increasingly smaller volumes of water is an important task in miniaturized microfluidic systems. However traditional mechanical approaches do not scale well to smaller volumes due to the increased importance of interfacial forces relative to inertial forces. Thus alternative methods to control liquid interactions with surfaces and to drive droplet motion are needed. We have previously demonstrated large photo-induced switching of contact angles (10-12 degrees) for water and other fluids on azobenzene-functionalized smooth Si surfaces. With these surfaces we find one can reversibly switch the surface wettability and in cases of sufficiently low hysteresis move liquid droplets by light-induced gradients in the surface tension. In this work, we extend these studies to the design of surface morphologies for increasing the effectiveness of photo-induced switching of surface wetting. We have fabricated ordered arrays of micrometer sized pillars (heights and spacing ~ 5 to 50 µm) on Si substrates. We also have prepared novel surfaces using CVD vapor-liquid-solid growth to fabrication surfaces with various lengths of Si nanowires (~50-100 nm in diameter) and combinations of nanowire-micropillar structures to form hierarchical arrays. By combining surface roughness with photochromic azobenzene monolayers, we demonstrate the amplification of the light-induced switching angle by up to a factor of 2 compared to smooth surfaces. Particularly effective amplification is found for hierarchical nanowire-micropillar designed surfaces. We discuss how such amplification enables increased control of surface wettability and droplet manipulation by optical means.

SS-ThP2 Surface Bonding Effects in Nanoparticles, ***H.H. Farrell***, *C.D. Van Siclen, D.M. Ginosar, L.M. Petkovic,* Idaho National Laboratory, *R.D. Parra*, DePaul University

The nature of the bonding at surfaces has a profound effect on their properties. Current models for the cohesive energy of nanoparticles generally predict a linear dependence on the inverse particle diameter, 1/r, for low aspect-ratio (spherical) clusters.@super1-4@ Although this is generally true for metals, we have recently found that for the Group IV semiconductors, C, Si and Ge, this linear dependence does not hold.@super5. Instead, using first principles, density functional theory calculations to calculate the binding energy of these materials, we find a roughly quadratic dependence on the inverse of the particle size. Similar results have also been obtained for the metallic Group IV elements Sn and Pb and for Mg, another "poor" metal.@super5@ This result is in direct contradiction to current assumptions. Further, as a consequence of this quadratic behavior, the melting point of these materials will not be linear in 1/r, but will experience less suppression than experienced by metal nanoparticles with comparable bulk binding energies. Similarly, the vapor pressure of semiconductor nanoparticles will rise more slowly with decreasing size than would be expected. This non-linearity also affects sintering or Ostwald ripening behavior of these nanoparticles as well as other physical properties that depend on the nanoparticle binding energy. The reason for this variation in size dependence involves the covalent nature of the bonding in semiconductors, and even in the "poor" metals. New work on other materials, including compound semiconductors and oxides will also be presented.

[1] See, for example, S. C. Vanithakumari, and K. K. Nanda, J. Phys. Chem. B 110, 1033 (2006), and references therein.

[2] See, for example, W. H. Qi, M. P. Wang, M. Zhou, and W. Y. Hu, J. Phys. D: Appl. Phys. 38, 1429 (2005), and references therein.

[3] See, for example, Chang Q. Sun, H. L. Bai, S. Li, B. K. Tay, C. Li, T. P. Chen, and E. Y. Jiang, J. Phys. Chem. B 108, 2162 (2004), and references therein.

[4] See, for example, M. Wautelet, J. P. Dauchot, and M. Hecq, J. Phys.: Condens. Matter 15, 3651 (2003), and references therein.

[5] H. H. Farrell and C. D. Van Siclen, accepted for publication in J.Vac. Sci. Technol. B.

SS-ThP3 Initial Adsorption of Yttrium on Si(001) 2X1 Surface, ***S.Y. Chiam***, Imperial College London, Singapore, *A.C. Huan,* Institute of Materials Research and Engineering, Singapore, *W.K. Chim,* National University of Singapore, *J. Zhang,* Imperial College London, Singapore, *J.S. Pan*, Institute of Materials Research & Engineering, Singapore

Initial adsorption sites of metal on Si is an increasingly important area of research especially for growth of thin films for low dimensional devices. Growth and simulation of heterojunction thin films on Si often require a more detail information about the position and bonding of the adatom. For instance, study of Sr with experimental and theoretical methods have lead to a better understanding of Sr adatom's preferred environment and gave insights into subsequent growth of epitaxial thin film, in particular, SrTiO3. In this work, we have investigated the initial adsorption of transition metal yttrium (Y) on Si(001). Y although formally a transition metal, have very similar valence electronic properties with the lanthanide family, including lanthanum. In Si based electronics, yttrium silicide, yttrium silicate and yttrium oxide are all potential thin films for source-drain contacts, infrared-detectors, and gate dielectrics. Furthermore, information about Y adsorption sites can aid in the design and growth of ternary or quaternary oxides (eg. LaYAl2O3). We have examined the real-time deposition of Y on Si(001) 2X1 by mounting a EFM evaporator source on the STM chamber. Therefore, we have observed the deposition of sub-monolayer coverage of Y atom on the same area of clean Si image thereby reducing any errors that might arise from adsorption of other species in UHV. Our work shows that yttrium adsorbs primarily on dimer bond instead of the cave site as predicted from a theoretical simulation of La on Si(001). We've examine the possible structure for such an adsorption and discuss about its stability and its bonding character using both STM and UPS.

SS-ThP4 Site Specific Chemisorption of Cl on Si(114), ***R.E. Butera***, *A. Agrawal, J.H. Weaver*, University of Illinois at Urbana-Champaign

The dissociative chemisorption of Cl on Si(114) was studied at room temperature using scanning tunneling microscopy (STM). Si(114) is a stable, planar, single-domain, high-index surface composed of rebonded atoms, dimers, and tetramers each aligned in rows along [-110]. STM imaging shows preferential Cl-termination of rebonded atom and dimer sites over tetramer sites. Moreover, the prevalence of specific chlorinated tetramer configurations reveals that dissociation is sufficiently exothermic that Cl can interrogate the potential energy landscape to find a local minimum. A 10 minute anneal at 550 K facilitates diffusion and allows the system to reach the equilibrium configuration. Sequential exposure and annealing cycles reveal a coverage-dependent site occupancy dictated by surface π-bonding. This study provides the necessary starting point for a thorough investigation of the structural implications of halogen etching where we find preferential desorption and novel pattern formation.

SS-ThP5 Irreversible Structural Transformation of Si(114)-2x1 Induced by Subsurface Carbon, ***G. Duvjir***, *H. Kim, J.M. Seo*, Chonbuk National University, Korea

From the previous STM studies of Si(114)-2x1, it had been reported that its pure and reconstructed surface (A-phase) is composed of rebonded restatom(R), tetramer(T), and dimer(D) rows. Recently, during annealing Si(114) near 1300C, we have found carbon-induced Si(114)-2x1 surface (B-phase) whose reconstruction is composed of T, T and D rows. Such a B-phase turns out to be induced by bulk carbon impurity segregated to surface and trapped at the subsurface. Once the surface changes from A-phase to B-phase, it does not return to A-phase by any kind of annealing process. The portion of B-phase relative to A-phase can also be increased by C2H2 adsorption on the clean substrate held at 500 C up to 100 percent. When the surface of B-phase is used as a substrate during Si-homoepitaxy or Ge-epitaxy, the overlayer thickness increases by two layers, differently from one-layer growth mode on the substrate of A-phase. It can be concluded that carbon having a stable subsurface site induces the anisotropic compressive stress on the surface, which results in insertion of Si-dimer to R row to form T row. The potential of this B-phase for application as a template is in its thermal stability and homogeneity since A-phase always has B-phase impurity even in the clean surface.

SS-ThP6 Evidences of Two Commuting Chain Structures Existing on Si(5 5 12)-2x1, ***H. Kim***, *H. Li, G. Duvjir, J.M. Seo*, Chonbuk National University, Korea

From STM/STS studies of the reconstructed Si(5 5 12)-2x1 surface, it has been found that its atomic structure of the unit-cell consists of four kinds of 1-D structures: honeycomb(H) chain, π-bonded chain, dimer-adatom(D/A) row, and tetramer(T) row. One (5 5 12) period is composed of three subunits, (337) unit with a D/A row [D(337)], (337) unit with a T row [T(337)], and (225) unit with both a D/A and a T row. Two kinds of adjacent subunits, T(337)/D(337) and D(337)/(225), are divided by H chains, while one kind of adjacent subunits, T(337)/(225), is divided by a π-chain. Existence of two chain structures has been confirmed as follows: (1)In the empty-state topographic image, H-chain has 2x periodicity along the chain due to buckling, while π-chain with missing atom defects has 1x periodicity. (2)From local STS measurement, the empty-state onset of π-chain is 0.5 eV smaller than that of H chain. (3)Exposed benzene molecule adsorbs selectively on π-chain. (4)In the homoepitaxy on Si(5 5 12)-2x1 at 550C, the first chain grown on D/A row is π-chain. Two chain structures commute with each other depending upon the external stresses perpendicular to the chain, which is the same for two row structures, D/A and T rows. These results indicate that, although numbers of consisting atoms and dangling bonds(DBs) of two different chains are identical, different DB directions induced by tensile stresses perpendicular to the chain result in such a distinct reactivity.

SS-ThP7 In-induced Atomic Chains on the Stepped Si Surface : In/Si(557)1x3, ***I. Song**, J.H. Nam, M.K. Kim, C.-Y. Park, D.H. Oh, J.R. Ahn*, Sungkyunkwan University, Korea

We have investigated the In-induced one-dimensional (1D) surface reconstruction on the Si(557) surface using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). One-dimensional electron systems have showed exotic phenomena such as Jahn-Teller distortion, non-Fermi liquid behavior, and Peierls instability.[1] Recently, stepped Si surfaces have attracted much attention as templates for formation of one-dimensional structures. Some examples that have been extensively studied are the Au/Si(553), Au/Si(557), Pb/Si(557) surfaces.[2] The In-induced 1D structure on the Si(557) surface was prepared by depositing In on the RT Si(557) surface and subsequent annealing at 500 °C. LEED show the In-induced surface reconstruction to have 1×3 phase, where the direction of the ×3 period is perpendicular to the step direction. In STM images, we found two kinds of atomic wires located at the step edge and within the terrace, respectively. The atomic chain within the terrace has obviously ×3 period along the chain direction, while the atomic chain at the step edge seems to have ×1 period along the chain direction. The atomic chains on the In-induced Si(557)1×3 is quite similar with those on the Au/Si(557) surface.[3] We will explain the In-induced Si(557)1×3 surface in comparison with the Au/Si(557) surface.

[1] J. R. Ahn, J. H. Byun, H. Koh, E. Rotenberg, S. D. Kevan, and H. W. Yeom, Phys. Rev. Lett. 93, 106401 (2004)

[2] J. N. Crain, J. L. McChesney, Fan Zheng, M. C. Gallagher, P. C. Snijders, M. Bissen, C. Gundelach, S. C. Erwin, and F. J. Himpsel, Rhys. Rev. B 69, 125401 (2004)

[3] M. Krawiec, T. Kwapinski, and M. Jalochowski, Phys. Rev. B 73, 075415 (2006).

SS-ThP8 Ozone Oxidation of Self-Assembled Monolayers on Silicon Surfaces, ***T.M. McIntire***, University of California, Irvine, *A.S. Lea, P.L. Gassman*, Pacific Northwest National Laboratory, *Q. Li*, KLA-Tencor Corporation, *O.S. Ryder, B.J. Finlayson-Pitts*, University of California, Irvine

Airborne particles have well-documented effects on human health, visibility and the chemistry of the atmosphere. A major area of concern, but also largely uncertain, is the impact of particles on global climate. A significant part of this uncertainty is the lack of understanding of the nature of the organic component. This deficiency includes the chemical speciation and the distribution of the organics between the surface and the bulk of liquid particles, as well as changes due to oxidation during transport in the atmosphere. In this work, the formation of large organic aggregates has been observed from the ozone oxidation of unsaturated alkene self-assembled monolayers (SAMs) on solid silica surfaces. Ozonolysis of terminal alkene SAMs of 3- and 8-carbon lengths, as proxies for organic-coated airborne dust particles, leads to the formation of large hydrophobic aggregates which do not increase the uptake of water as previously assumed. These SAMs were generated on silicon substrates and reacted at room temperature with gaseous ozone. A combination of experimental techniques, atomic force microscopy, scanning electron microscopy, Auger microprobe, time-of-flight secondary ion mass spectrometry, and transmission FTIR, were used to study the surface composition and morphology after oxidation. Large (micron-size) organic aggregates formed on the surface while the surrounding substrate became depleted of carbon and exposed the original substrate. This highly unusual result establishes that the mechanism of ozonolysis of alkene SAMs involves polymerization, likely induced by secondary reactions of the Criegee intermediate (CI). For that reason, formation of polymers under atmospheric conditions may be more common than previously recognized. The uptake of water was not increased upon oxidation of these films, in contrast to current expectations. Implications for SAM reactions and stability in air, ozonolysis of alkenes on surfaces, and for the oxidation of alkenes on airborne dust particles are discussed.

SS-ThP9 Thermal and Non-thermal Interactions of MEA on Si(100), ***B. Forster**, S. Yeninas, J. Thompson, J.H. Craig, Jr., J. Lozano*, Bradley University

We have used several surface analysis techniques to study the adsorption dissociation, and desorption of monoethylamine (MEA) on Si(100) surfaces. Thermal processes were studied using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). Non-thermal processes using electron irradiation of MEA/Si(100) at 100 K were studied using HREELS TPD, x-ray photoelectron spectroscopy (XPS), and electron stimulated desorption (ESD). Our data indicated low temperature electron-induced dissociation of MEA, deposition of nitrogen, and formation of silicon nitride.

SS-ThP10 Adsorption Studies of Trisilylamine on the Si(100) Surface, ***B. Bush**, A. Marquis, O. Egwu, J.H. Craig, K. Roos, J. Lozano*, Bradley University

Trisilylamine $(SiH_3)_3N$ is the silicon analog to the carbon-containing molecular species trimethylamine $(CH_3)_3N$. The fundamental structural difference between these amines is the planar backbone exhibited by TSA. The Si_3N backbone is the same structure which occurs in silicon nitride Si_3N_4. Little fundamental work has been reported on the adsorption properties of TSA on the Si(100) surface. We report on the results of a series of adsorption studies of TSA on the Si(100) surface at 100K using XPS, UPS, HREELS, and TPS to elucidate the dissociation pathways and bonding of the TSA molecule on the surface. Results of electron bombardment studies to remove hydrogen ligands from the adsorbed species will also be discussed. Preliminary STM images of very low coverage adsorption of TSA on the Si(100) surface will also be presented and discussed.

SS-ThP11 STM Study of Niobium Deposited on Si(111) Surface, ***H. Suh**, Y. Kuk*, Seoul National University, Korea

Superconductivity in low dimensionality has been attracting attentions of many researchers due to its technological and scientific importance. While it is well known that superconductivity is suppressed as the dimensionality is reduced, the conditions and criteria for the dimensionality still remain questionable. Scanning Tunneling Microscopy is a powerful tool for studying both topographies and local electronic structures in nanometer scale. To explore superconductivity at reduced dimensionality, we studied Nb deposits on Si surfaces. Nb, which has the highest superconducting transition temperature among elemental superconductors and has various compounds with even higher transition temperatures, was e-beam evaporated onto Si(111) surface and annealed. The surface was characterized with Scanning Tunneling Microscope (STM) and local electronic structures of the deposited Nb was studied with Scanning Tunneling Spectroscopy (STS).

SS-ThP12 STM Study of Submonolayer of Au Adsorption on Si (111)-(7x7) Surface and Influence of Substrate Temperature, ***H. Shim**, L. Zhang, Y. Kim, G. Lee*, Inha University, South Korea

Adsorption of submonolayer Au on Si (111)-(7x7) surface at different substrate temperature was investigated using STM. At room temperature deposition, the Au adsorption on Si (111)-(7x7) typically features coexistence two species, high-lighted triangles and clusters confined within half-unit cells. The high-lighted triangles are dominant at a very low coverage, but give way to clusters with various sizes as the coverage increases. Slightly heating the substrate (below 150 C) during deposition also decreases the number of the highlighted triangles. The clusters, mostly confined within half unit cells for the deposition at substrate temperatures below about 350 C, coalesce to cover the borders of the half unit cells when substrate temperature increases. Vacancies and disorders are created near the clusters, suggesting the incorporation of Si atoms into the clusters at the heated substrate. At about 550 C deposition, the Au adsorption leads (5x2) reconstruction in the form of characteristic island-hole pairs on terrace or only (5x2) islands at the step edge. The evolution of the Au-adsorbed surfaces with substrate temperature during deposition will be discussed and compared with that of the room temperature deposition and post annealing.

SS-ThP13 Controlling and Probing Molecular Orientation and Differential Conductivity in Solid Films of Ionic Perylenebis(dicarboximide)s, ***A. Jeewandara**, S.M. Casey*, University of Nevada, Reno

We report the control of molecular orientation and differential conductivity in solid films through self-organization and induced orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide and derivatives and formed chromonic N phases (nematic lyotropic liquid crystalline phases) at room temperature upon solution concentration. Upon induced alignment (by shearing) of the chromonic N phase on a substrate and removal of solvent, anisotropic solid films of the dichroic dyes were produced. By use of a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films was determined to be perpendicular to both the shearing direction and the substrate plane. The effect of molecular orientation on the differential conductivities in the films will be discussed.

SS-ThP14 The Molecular Scale Origins of the Surface Memory Effect, *K. Bufkin, R. Adams, B.L. Johnson, D.L. Patrick*, Western Washington University

The behavior of liquid crystals (LC) at interfaces has been an important area of research for many years because of its relevance to LC device applications such as LCDs. In this research ordered monolayer films of the LC 4'-octyl-4-biphenyl-carbonitrile (8CB) on highly oriented pyrolytic graphite were investigated by scanning tunneling microscopy (STM) in order to study their disordering kinetics and to develop a better understanding of a phenomenon known as the surface memory effect. The surface memory effect occurs when a LC film retains a degree of remnant orientational order even after being heated above its isotropic transition temperature. Using STM we studied molecular-scale ordering in 8CB films heated to varying temperatures and for varying lengths of time. The results are compared to large-scale Monte Carlo simulations of a 2-dimensional Ising Model, which suggests for the first time that nearest-neighbor interactions in the isotropic phase play an important role in producing surface memory effects.

SS-ThP15 Chiral Control in Organic Monolayer Films Using Liquid Crystal Solvents, *C. Reinhart, A. Morris-Cohen, D.L. Patrick*, Western Washington University

Many important chemical and physical properties of organic thin films are affected by molecular-scale order. We present investigations of a method for controlling the orientation of molecules and their chirality in monolayer films using thermotropic liquid crystal (LC) solvents and magnetic fields. Two different methods of chiral and orientational control will be discussed. The first involves an achiral set of organic compounds that, when deposited on a graphite surface, produce crystalline monolayers with non-superimposable left and right handed domains; the second set involves 3-dimensionally chiral compounds and is aimed at controlling enantiomeric excess through selective adsorption. Molecular ordering, 2D chirality and enantiomeric excess are analyzed by scanning tunneling microscopy.

SS-ThP16 Organic Semiconductor Film Growth Using Liquid Crystal Solvents, *B.B. Ohlson, F.S. Wilkinson, D.L. Patrick*, Western Washington University

Organic semiconductor (OS) thin films have attracted widespread interest for their potential use in electronics, optics, information storage, photovoltaics and many other applications. Since properties such as charge transport are known to be anisotropic in most crystalline structures, having control of crystallite orientation should lead to improvements in the tunability of devices such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs). Furthermore, by creating films that are highly crystalline, with large grain size, and thus less potential for charge trapping at the grain boundaries, charge transport characteristics can be optimized. We present a new approach for growing OS thin films using thermotropic nematic liquid crystal (LC) solvents to deposit tetracene films with long-range uniaxial order. The LC solvent imprints its directionality onto the crystalline tetracene film as it grows, resulting in larger, highly oriented crystals. Films were deposited via atmospheric-pressure sublimation onto substrates coated by a LC layer oriented using mechanically rubbed polyvinyl alcohol (PVA). This poster will describe the effects of different processing conditions, such as LC layer thickness, substrate temperature and flux rate on film morphology and crystallinity.

SS-ThP17 Analyte Binding to CoPc: A Comparison of Analyte Binding Strength and Basicity, *N.L. Tran, A.C. Kummel*, University of California at San Diego

A recent study has shown a strong correlation between analyte electron donor ability and chemiresistive Cobalt phthalocyanine (CoPc) sensor response.[1] The -H_{BF3} scale method was used as a measure of the electron pair donor ability of the 10 analytes investigated.[2] It is speculated that sensor response is dictated by the degree of charge transfer in CoPc-analyte complexes as opposed to analyte binding strength. To investigate this hypothesis, the binding strength of these electron donating analytes (acetonitrile being the weakest and triethylamine the strongest electron donor) to the Co metal of CoPc was calculated using density functional theory. Subsequently, the atomic charges of the CoPc and CoPc-analyte complex will be analyzed to measure the degree of charge transfer between the analyte and Co metal. The interaction of a neurotoxin analogue, dimethyl methylphosponate (DMMP) with CoPc is also being investigated to determine the potential for use of CoPc sensors to detect organophosphate neurotoxins. Preliminary DFT simulations show that although O_2 binding to the Co metal is weak (less than -0.1 eV exothermic), a large effect on the CoPc electronic structure and charge transfer is observed. Weak analyte-MPc binding with a large change in electronic structure are the key properties of a good sensor because a reversible absorption will result in a large change the conductivity of the MPc film.

[1] F. Bohrer, A. Sharoni, C. N. Colesniuc, J. Park, I. K. Schuller, A. Kummel, and W. C. Trogler, Journal of the American Chemical Society submitted (2007).

[2] P. C. Maria and J. F. Gal, Journal of Physical Chemistry 89 (7), 1296 (1985).

SS-ThP18 Ablation of Polyvinylidene Fluoride at 157-nm[1], *J.A. Leraas, S.R. John, S.C. Langford, J.T. Dickinson*, Washington State University

Polyvinylidene fluoride [PVDF—(CH $_2$CF$_2$)$_N$] is a piezoelectric polymer employed in a variety of sensors. PVDF also possesses excellent thermal and chemical stability, which complicate the manufacture of parts with complex geometries. Structure formation by energetic radiation is potentially important to the broader application of this material. In this work, we characterize the products produced by exposing PVDF to 157-nm radiation from an F_2 excimer laser. In the early stages of irradiation, the dominant neutral product is HF, produced by photochemical excitation of side chain bonds. HF production is accompanied by the conjugation of C-C bonds and cross-linking. Given sufficient laser fluences, prolonged exposure produces bursts of positive and negative charge, neutral particles, and light. We attribute burst formation to the accumulation of conjugated carbon bonds in the near surface region. When the peak temperatures generated by successive laser pulses reach a critical level, a burst results. This unusual behavior is associated with the chemistry of the PVDF molecule. In polytetrafluorethylene, for instance, 157-nm radiation cleaves the polymer backbone to produce small fragments that are continuously removed from the target. Side chain cleavage in PVDF allows damaged material to accumulate until conditions produce a large burst of emission. The charged products accompanying a burst are strongly coupled to form a tenuous plasma, or charge cloud. The positive ions in the charge cloud have kinetic energies of 7-10 eV, consistent with electrostatic ejection from the polymer surface. We show evidence for high electron densities in the charge cloud—sufficient to neutralize most (but not all) of its positive charge. These electrons are largely confined to the charge cloud, and play an important role in generation of negative ions by dissociative electron attachment to neutral species. The relatively high velocity of the charge cloud is matched only by the fastest neutrals. Therefore only the fastest neutral particles are vulnerable to attachment. The spatial and temporal distribution of the product species have important consequences on product evolution prior to deposition. The unsteady emission intensities, with occasional large bursts, provide challenges and opportunities for the growth of PVDF films by laser ablation at 157 nm.

[1] This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP19 Ablation Mechanism In Polytetrafluoroethylene (PTFE) under 157-nm Irradiation[1], *S.R. John, J.A. Leraas, S.C. Langford, J.T. Dickinson*, Washington State University

Polytetrafluoroethylene (PTFE) (C2F4)n is a model organic polymer with unique properties. In this work, we explore the mechanisms responsible for the superior etching others have demonstrated using 157-nm F2 excimer lasers. At fluences well below the threshold for plasma formation, the major neutral products are (CF2)x units. Thus decomposition is primarily from backbone scission. Mass selected time-of-flight signals for these neutral products show a fast component with energies on the order of 1.2 eV, as well as a slower, thermal component. We attribute the fast component to products formed from scission of C-C bonds due to electronic excitations along the surface. We attribute the slower component to products produced in the bulk, which then diffuse to the surface and desorb. The clean etching of PTFE at 157 nm is the result of dissociative electronic excitations. Nevertheless, analysis of the slow component indicates high surface temperatures. The F2 laser significantly heats the surface. Intense electron, positive and negative ion emissions are also observed. The high positive ion kinetic energies (3-10 eV) are consistent with an electrostatic emission mechanism. The negative ion signals are an order of magnitude weaker than the positive ions, but display similar kinetic energies (3-5 eV). We attribute negative ion formation to dissociative electron attachment of neutral monomers. This process requires high electron densities, which are observed in the cloud of positive ions. The presence of both positive and negative ions, in addition to reactive (CF2)x units, would promote the growth of high quality PTFE films by laser ablation deposition. We will briefly describe the ablation of a another fluorocarbon polymer, polyvenylidenefluoride (PVDF) (C2H2F2)n, at 157-nm. Initial exposure yields intense emissions of neutral HF due to side chain scission-in contrast to PTFE, where fragmentation is predominately due to backbone scission. The presence of hydrogen in the PVDF renders side chain bonds especially vulnerable. During prolonged irradiation, especially intense bursts of charged and neutral products accompany some laser pulses and not others.

The bursts are presumably due to the accumulation of damaged material in the intervening laser pulses.

[1] This work was supported by the U.S. Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP20 Solid-Liquid Interface Engineering: Static and Dynamic Hydrophobicities on Self-assembled Monolayer Surfaces, *N. Yoshida*, The University of Tokyo, Japan, *S. Suzuki,* Tokyo Institute of Technology, Japan, *M. Sakai, A. Hashimoto,* Kanagawa Academy of Science and Technology, Japan, *Y. Kameshima, A. Nakajima,* Tokyo Institute of Technology, Japan, *T. Watanabe*, The University of Tokyo, Japan

Wettability of solid surface has attracted much attention in many fields, from basic surface science to practical uses. Up to now, numerous studies have sought to interpret the static hydrophobicity (contact angle of a droplet and surface energy/surface tention of soild surface) in terms of the interaction between liquid and solid surface. The static hydrophobicity has been well-clarified (controlled by surface energy and morphology), however, the dynamic hydrophobicity (sliding angle and velocity of a droplet), a measure of dynamic adhesive property against water, is still in controversy. Practically, dynamic hydrophobicity does not simply depend on static hydrophobicity. Thus far, no one could completely explain a fact that hydrophobic surfaces of similar water contact angles often show quite different adhesive property against water. In this study, we successfully prepared various hydrophobic surfaces using alkyl and fluoroalkyl silanes with various adhesive properties against water in terms of solid-liquid interface engineering. We will demonstrate that the dynamic hydrophobicity, a measure of the adhesive property against water, depended on the surface morphology (even of the order of a few nanometers) and surface composition (small amount of polar groups on the surface) and that we could control it independent of static hydrophobicity.

SS-ThP21 Structural, Mechanical and Electronic Properties of Stilbene and Pentathiophene Based Molecular Monolayers, *Y. Qi*, University of California, Berkeley, *B. Hendriksen, V. Navarro, D. Esteban, J.Y. Park, I. Ratera, J. Klopp,* Lawrence Berkeley National Laboratory, *C. Mauldin,* University of California, Berkeley, *C. Edder,* Lawrence Berkeley National Laboratory, *J. Frechet,* University of California, Berkeley, *M. Salmeron*, Lawrence Berkeley National Laboratory

The incorporation of molecules in electronic devices is promising for technological applications and a new direction in fundamental research. The structural, mechanical and electronic properties of manolayers of two molecules containing pi-systems have been studied with conducting probe atomic force microscope (CP-AFM), X-ray photoemission spectroscopy (XPS) and near edge X-ray fine structure spectroscopy (NEXAFS). One is w-(trans-4-stilbene)alkylthiol, and the other is decyl-pentathiophenyl butyric acid. We found that the w-(trans-4-stilbene)alkylthiol molecules self-assemble on Au (111) with the thiol group covalently bond to Au surfaces as confirmed by X-ray photoemission spectroscopy. The molecular film undergoes a slow structural change from a tilted to a more upright geometry, a process that can be accelerated by thermal annealing. In all cases w-(trans-4-stilbene)alkylthiol molecules show poor electrical conductivity in the vertical direction. Molecular monolayers of decyl-pentathiophenyl butyric acid were deposited on heavily doped Si (100) by the Langmuir Blodgett technique. The orientation of the molecules has been studied by NEXAFS. Current versus voltage measurements and conductivity mapping reveal a higher conductivity than that of w-(trans-4-stilbene)alkylthiol self-assembled monolayers. The friction and the conductivity were observed to strongly depend on the molecular arrangement.

SS-ThP22 Characterization of Chemically Etched Poly(tetrafluoroethylene), *T.R. Richardson*, *F.A. Donate, C.L. Gentry, D.D. Hawn, B.J. Kern, G.E. Mitchell, G.E. Potter, C.W. Reinhardt, R.J. Wachowicz,* The Dow Chemical Co., *S. Marsh, M.E. Yevich*, Acton Technologies

Chemical etching solutions are typically employed to prepare the surface of poly(tetrafluoroethylene) for bonding to a surface. These etching solutions are based on sodium-naphthalene complexes in an aprotic organic carrier such as a glycol diether. The use of such etchants produces a chemically modified surface suitable for bonding. We employed X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and atomic force microscopy in order to understand the chemical properties of these etched surfaces. Key to this work was a procedure which utilizes macrotomy to remove thin layers of material from the surface, but these sections are obtained at a very low angle relative to the surface plane (1° or 1/2°). Using this procedure, the thickness of a layer could be "magnified" 60 or 120 times. This facilitated the use of XPS and SIMS to analyze the surface composition as a function of depth. The procedure developed produced surfaces and thin sections with no measurable smearing or contamination. The design of the apparatus resulted in production of sections or surfaces with reproducible and accurate appearance and chemistry. In this presentation we will discuss the results obtained from these low angle macrotomed surfaces, highlighting the chemistry of the surface and the modified zone. The results discussed apply to molded industrial poly(tetrafluoroethylenes).

SS-ThP23 Surface Chemistry of (2,4-dimethylpentadienyl) (ethylcyclopentadienyl)Ru on Polycrystalline Ta, *K.M. Thom*, *J.G. Ekerdt*, University of Texas at Austin

As device dimensions in integrated circuits scale down, there is a need to deposit ultra-thin, conformal, continuous films for various microelectronic applications. Ruthenium (Ru) thin films are promising candidates for applications such as diffusion barriers in copper metallization and capacitors in dynamic random access memories. Chemical vapor deposition and atomic layer deposition have been used to deposit Ru thin films using a variety of precursors, but the surface chemistry of these precursors is largely unexplored. This work examines the surface chemistry of (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)Ru [DER] on a polycrystalline tantalum (Ta) foil, with and without the presence of methyl iodide. X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) were used to study the adsorption and desorption behavior. Because DER was found to dissociate negligibly at room temperature and above, low temperature experiments were used to examine the interaction of the DER with the Ta foil. The DER was dosed onto Ta at 140 K and then desorbed during the TPD process; XPS spectra were taken both before and after TPD. The DER adsorbs and desorbs molecularly, although a small amount of dissociation occurs during TPD. Both XPS and TPD results indicate that the DER saturates on the surface at an exposure of about 4 Langmuir (L); no multilayers are formed. For exposures up to 0.5 L, a single TPD desorption state is observed at 272 K. As coverage increases, the single state splits into two desorption features which are centered at 264 K and 297 K at saturation. The two states are attributed to different physical states of the molecules; possibly two different molecular orientations occur on the surface. The Ru $3d_{3/2}$ XPS feature shifts from 286.2 eV to 287.3 eV as exposure is increased from 0.1 L to saturation, a binding energy (BE) change of about 1 eV; the Ru $3d_{5/2}$ XPS feature also shifts up by 1 eV. The BE shift with increasing coverage is consistent with the presence of two adsorbed states. Because other research has shown alkyl iodides enhance the nucleation of Ru films, methyl iodide was co-dosed into the chamber along with the DER in an attempt to promote dissociation at room temperature and above. The addition of methyl iodide enhanced the dissociation of DER as compared with the molecule alone. This talk will discuss the surface reactions of DER in the presence and absence of adsorbed iodide.

SS-ThP24 X-Ray Photoelectron Spectroscopy for Impedance Measurements, *S. Suzer*, *H. Sezen, G. Ertas, A. Dana*, Bilkent University, Turkey

A new technique is introduced for probing charging/discharging dynamics of dielectric materials, in which X-ray photoemission data is recorded while the sample rod is subjected to 10.0 V square-wave pulses with varying frequencies in the range of 0.001 to 1000 Hz. This technique allows us to probe electrical impedance of dielectric materials. Accordingly, for a conducting graphite sample the C1s peak appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) with no frequency dependence. However, the corresponding C1s and O1s peaks of polymeric materials (PS, PMMA, and PS/PMMA blends) appear with less than 20.0 eV difference and exhibit strong frequency dependence due to charging of the polymeric films, which are faithfully reproduced by a theoretical model.[1,2] Information can be obtained from the frequency dependence of the positions, as well as the widths of the peaks. Various applications of this technique for characterization of organic (polymeric) and inorganic homogeneous and heterogeneous materials and surface structures will be presented and discussed.

[1] S. Suzer, and A. Dana, J. Phys. Chem. B 110, 19122 (2006).

[2] H. H. Sezen, G. Ertas, A. Dana, and S. Suzer, Macromolecules (in press).

SS-ThP25 Sliding Behavior of a Water Droplet between Two Hydrophobic Coatings by Self-assembled Monolayer, *A. Nakajima*, *S. Suzuki*, Tokyo Institute of Technology, Japan, *M. Sakai, A. Hashimoto,* Kanagawa Academy of Science and Technology, Japan, *N. Yoshida,* The University of Tokyo, Japan, *Y. Kameshima, K. Okada*, Tokyo Institute of Technology, Japan

Self-assembled monolayer (SAM) coatings of organosilanes have been widely used for surface modification of inorganic materials. We studied the sliding behavior of water droplets sandwiched between Si substrates treated by octadecyltrimethoxysilane (ODS) and fluoroalkylsilane (FAS) by changing the plates' distance (D) and droplet mass (m). The sliding angle depended on D, m, and the upper and bottom combination of the coating. The droplet between FAS coatings exhibited larger sliding angle than the

ODS coating when D=1.0 mm although the FAS coating possesses higher water contact angle. The sliding behavior of water droplets sandwiched between ODS and FAS coatings was observed using a high speed camera system on a declined surface (35 degrees). The larger droplet mass and plate distance, the larger sliding acceleration. The internal fluidity in the droplet visualized by particle image velocimetry method revealed that the droplet slid down with twin flows between plates and that their border was almost the center of the plates. The water droplet sandwiched between FAS/ODS exhibited heterogeneous rolling fluid: the border of the twin flow was not the center between the plates. The magnitude of the rolling fluid depended on the surface chemical composition and the distance between two plates.

SS-ThP26 Characterisation of Self-Assembled Monolayers Using Angle Resolved XPS, ***J. Wolstenholme***, Thermo Fisher Scientific, UK, *D.J. Graham*, Asemblon, Inc., *R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMS) are increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The length of many of the molecules used in these layers and, therefore, the thickness of the monolayers formed by them is often less than the attenuation length of the photoelectrons emitted in the XPS process. This means that the XPS technique is ideal for characterising the layers. The additional benefits coming from ARXPS are also important for the determination of layer orientation and thickness. For this work, the ARXPS data was collected in parallel over a 60 degree range, without the need to tilt the samples. This means that it is possible to collect angle-resolved XPS maps of the surface to examine the uniformity of the layers. If the layers are uniform, data can be collected as a map over a large area to minimise the X-ray flux density used in the analysis. By examining a number of samples having the same SAM at the surface, the precision of the measurements can be determined. Obviously, high precision is required if the two-dimensional uniformity is to be investigated. It will also be shown, using a range of SAM's, that the techniques developed for extracting non-destructive depth profiles from ARXPS data can be successfully applied to these materials. Results will be reported from SAMs formed from alkane thiols and from molecules containing additional functional groups.

SS-ThP27 Study of the Interplay between PDMS and Surfaces Modified with Monolayers and Small Molecules, ***L. Yang***, *F. Zhang*, Brigham Young University, *N. Shirahata, T. Nakanishi*, National Institute for Materials Science, Japan, *M.R. Linford*, Brigham Young University

Here we describe a method for probing the surface free energies of materials by stamping them with polydimethylsiloxane (PDMS) stamps that have also been wet with low molecular weight PDMS. Hydrophobic surfaces, e.g., alkyl monolayers with high advancing water contact angles, resist adsorption of PDMS, while PDMS adsorbs effectively onto hydrophilic or even moderately hydrophobic surfaces. For example, PDMS transfers to thin films of C60, while it does not transfer to thin films of molecules that contain long alkyl chains. In addition, PDMS transfers to hydrophilic spots patterned onto hydrophobic monolayers, but not onto the background. The degree of PDMS transfer can be used to monitor processes such as the contamination of a clean metal surface in the ambient. The PDMS transferred in these cases is easily detected by spectroscopic and imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) because of the sensitivity of this technique for this species. Wetting, X-ray photoelectron spectroscopy, and principal components analysis of the ToF-SIMS data are also employed to study this problem.

SS-ThP28 Direct Polymer Growth on Hydrogen-Terminated Silicon, ***M.R. Linford***, Brigham Young University, *N. Shirahata*, National Institute for Materials Science, Japan, *R.B. Blake, M.V. Lee*, Brigham Young University

When hydrogen-terminated silicon is immersed in a solution of an unsaturated monomer and a free radical initiator, a very thin, ca. 2 nm, thin polymer film grows on the surface, provided the temperature of the reaction mixture is raised to the decomposition point of the initiator. Changing the nature of the monomer, the initiator, and reaction conditions do not seem to lead to the production of significantly thicker polymer layers. However, addition of appropriate chemical reagents allows ca. 10 nm polymeric layers to be directly grown on hydrogen-terminated silicon. This method can be used in conjunction with photopatterning of hydrogen-terminated silicon, which removes hydrogen termination in certain areas on the surface and thus prevents polymer growth in these regions. Surface reactivity and patterning are confirmed by X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy.

SS-ThP30 In Situ Real-Time Grazing Incidence Study of Organic Thin Film Growth, ***A. Amassian***, *V.A. Pozdin, S. Bhargava*, Cornell University, *D.-M. Smilgies*, CHESS, Cornell University, *A. Papadimitratos, S. Hong*, Cornell University, *A.R. Woll*, CHESS, Cornell University, *G.G. Malliaras, J.R. Engstrom*, Cornell University

We have performed in situ, real-time grazing incidence X-ray synchrotron measurements during the growth of organic thin films of pentacene. Experiments were carried out on films deposited from both thermal and supersonic sources on a variety of substrates (e.g., SiO_2, photoresists, polymers) and over a broad range of process parameters (e.g., growth rate, temperature, beam kinetic energy). A CCD detector captured both in-plane Bragg peaks and out-of-plane Bragg sheets, allowing us to solve the 3D structure of pentacene crystals. We reveal the formation of new polymorphs of the so-called "thin film" and bulk phases of pentacene, while in situ measurements (video to be shown)provide new insights into the initial growth of organic crystals.

SS-ThP31 Self-Assembled Monolayers of Aromatic Tellurides on Gold and Silver Substrates, ***M.T. Weidner***, University of Washington, *A. Shaporenko*, Universität Heidelberg, Germany, *J. Müller, M. Höltig, A. Terfort*, University of Marburg, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of tellurolates are promising alternatives to most frequently used thiolate-based systems. In this study we present first experimental data on SAMs of aromatic tellurolates. These SAMs were fabricated on Au(111) and Ag(111) substrates from a ditelluride precursor, bis(4'-methylbiphenyl-4-yl) ditelluride (BBPDTe) and characterized by high resolution X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. BBPDTe was found to adsorb dissociatively on both substrates, resulting in the formation of well-defined, densely packed, and ordered BPTe SAMs, with a larger molecular inclination, a lower packing density, and inferior crystallinity on Au than on Ag. However, both BPTe/Au and BPTe/Ag were not stable under ambient conditions, but underwent a rapid autooxidation, which affected exclusively the tellurolate headgroups. The BPTe molecules in the oxidized films remained, however, bound to the substrate by the terminal O atoms coordinated to the Te moieties, and the quality of the films, given by parameters such as packing density, degree of the orientational order, and average tilt angle of the SAM constituents was not noticeably affected by the autooxidation. In addition, the BPTe SAMs were compared with the analogous thiol- and selenol-based systems, and common tendencies for the different chalcogen headgroups, ranging from Te to O, were derived.

Surface Science

Room: 608 - Session SS1-FrM

Surface Dynamics

Moderator: A.L. Utz, Tufts University

8:00am **SS1-FrM1 Formation and Dynamics of Sputter Ripples on an Epitaxially Grown Au Surface**, ***K. Mitchell***, *A. Yazdi, N. Ingle, T. Tiedje*, University of British Columbia, Canada

Under bombardment by a rastered 30keV Ga^+ ion beam, a flat epitaxially grown Au surface is found to exhibit the well known sputter ripple instability as first observed by Bradley and Harper.[1] These ripples exhibit a characteristic lateral length scale on the order of 100nm and a short-range RMS saturation height on the order of 10nm after receiving a fluence of approximately 1500 ions/nm^2. The starting surface is grown under UHV at 350°C on a freshly cleaved mica substrate resulting in a 0.5µm film with flat areas up to 8µm^2 having an RMS roughness of 0.5nm. Accurate topography data are gathered using ex situ AFM on areas exposed to increasing ion fluence to track the increase in roughness associated with the pattern formation, while in situ SEM imaging is used to observe the dynamics before and after the ripples have formed. These experimental data are compared to 2D numerical solutions of a non-linear partial differential equation which captures the essential features of height saturation, characteristic length scale and parabolic ripple shape. A state of the art fourth-order "exponential time differencing" method as perfected by Kassam and Trefethen[2] is used to advance the solution in time while high accuracy spectral methods are used to compute spatial derivatives. The equation is similar to the chaotic Kuramoto-Sivashinsky equation, but with an additional higher order non-linear term as derived by Castro and Cuerno.[3] Like the Kuramoto-Sivashinsky equation, linear terms of competing stability set the initial characteristic length and growth rate, while the non-linear terms are responsible for the height saturation and the surface shape. The additional non-linear term causes an increase in the characteristic time, length and height scales after saturation has occurred. By adjusting the strength of the new non-linear term, the solutions can be tuned to match the morphology of the experimentally observed surface. The resulting equation parameters are then able to give information about the physical constants involved in the experiment.

[1] Bradley, Harper, J. Vac. Sci. Technol. A 6,2390 (1988)
[2] Kassam, Trefethen, SIAM J. Sci. Comp. 26, 1214 (2006)
[3] Castro, Cuerno Phys. Rev. Lett. 94, 016102 (2005)

8:20am **SS1-FrM2 Charge Transfer Dynamics in Alkanethiolate Self-Assembled Monomolecular Films**, ***M. Zharnikov***, Universität Heidelberg, Germany, *S. Neppl*, Technische Universität München, Germany, *A. Shaporenko*, Universität Heidelberg, Germany, *U. Bauer, D. Menzel*, Technische Universität München, Germany, *P. Kao, D. Allara*, Pennsylvania State University, *P. Feulner*, Technische Universität München, Germany

Whereas static conductance of molecules arranged in self-assembled monolayers (SAMs) has been extensively studied, less is known about the dynamics of the charge transfer in these systems. We show that the latter phenomena can be successfully addressed by resonant Auger electron spectroscopy, using the core hole clock (CHC) method. For the test system, nitrile-substituted alkanethiolate SAMs, we obtained clear, quantitative results on the characteristic transfer time of the resonantly excited electron along the molecular chain to the conductive substrate in good agreement with theory. As compared to previous studies, the charge transfer pathway in our experiment was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the alkyl backbone. This particular tailgroup occurs to be a good candidate for such studies because of a suitable core hole lifetime (CLT) and the large contrast between resonant and non-resonant core decay spectra. The approach, used by us, avoids any contact and reproducibility problems and, by selection of suitable ligands with appropriate values of CLT and resonance position, spans a wide dynamic range. Extension to other functional groups is possible and promises to become a very valuable new source of information on charge dynamics in layers important for molecular electronics.

8:40am **SS1-FrM3 Dynamics of Analyte Binding onto a Metallophthalocyanine: NO/FePc**, ***S.R. Bishop***, *N.L. Tran, G.C. Poon, A.C. Kummel*, University of California, San Diego

The investigation of the gas-surface reaction dynamics of NO with an iron phthalocyanine (FePc) monolayer utilizing King and Wells sticking measurements is reported. The initial sticking probability is determined to be a function of both incident molecular beam energy (0.09 - 0.4 eV) and surface temperature (100 - 300 K). NO adsorption onto FePc saturates at 3% of a monolayer (ML) at all incident beam energies and surface temperatures suggesting that the final chemisorption site is confined to the iron metal centers. 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. The results are consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the aromatic periphery followed by diffusion to the Fe metal center. It is determined the NO molecule adsorbs to the FePc monolayer via a multiple pathway precursor-mediated chemisorption mechanism. The absorption mechanism of NO onto FePc was confirmed by control studies of NO sticking onto metal-free H_2Pc, inert Au(111), and reactive Al(111).

9:00am **SS1-FrM4 Atomic Scattering as a Probe of Polymer Surface and Thin Film Dynamics**, ***M.A. Freedman****, *S.J. Sibener*, The University of Chicago

We have studied the vibrational dynamics of self-assembled monolayers (SAMs) and polymer thin films, two complex systems of great technological interest, using the highly surface-sensitive and non-perturbative technique of low-energy helium atom scattering. While this technique has traditionally been used for single crystals and simple adsorbates on crystals, recent work in our group and elsewhere has expanded these studies to ordered organic monolayers. We have further broadened the range of studies performed with helium atom scattering to determine how much information can be gleaned from soft, disordered systems. We have shown that this technique provides a novel means for studying surface vibrational dynamics at these complex interfaces. We explored the interaction between the alkanethiol chains of the SAMs and the Au(111) substrate by investigating the energy of single phonon modes as a function of chain length. The fact that the observed phonon mode is dispersionless and exhibits no dependence on chain length indicates that the interaction between the adsorbate and substrate in the sagittal plane is dominated by single-chain harmonic-oscillator-type interactions. The energy of the single-phonon mode of decanethiol is larger than other chain lengths because its commensurate structure to the reconstructed Au(111) surface leads to stronger binding. We investigated the polymer thin film interface to determine the effect of nanoconfinement and polymer species on the vibrational dynamics. We find that helium atom scattering is a sensitive probe of the effect of nanoconfinement on the surface dynamics of poly(methyl methacrylate) (PMMA). Specifically, a reduction in the mean-square displacement derived from the elastic scattering and the reduced propensity for annihilation events in inelastic spectra indicate that thinner films are stiffer, perhaps due to substrate interactions. The inelastic spectra of PMMA, polystyrene, and polybutadiene have similar rates of intensity decay and absolute values of full width half maximum with increasing surface temperature. Deviations from a semiclassical scattering model and the linear increase in full width half maximum with increasing surface temperature indicate changes in the vibrational dynamics. We have shown that helium atom scattering is a sensitive probe of complex systems and may indeed give insight on whether the onset of glassy dynamics in the bulk affects dynamics at the topmost interface.

9:20am **SS1-FrM5 Local Electronic Properties of Molecular Assemblies at Surfaces**, ***J.I. Pascual***, Freie Universität Berlin, Germany **INVITED**

The electronic properties of inorganic functional materials can be understood and predicted from a conceptual knowledge of electron dynamics. However, when organic molecules are to be used in electronic devices an atomistic picture of molecular bonding is additionally required. Local phenomenology occurring at the nanoscopic scale related with molecular chemical bonding, and hence with electronic coupling, governs many of the mesoscopic properties of organic devices. On the one hand organic-inorganic bonding can be more relevant than the molecular functionality itself. On the other, intermolecular interactions play a key role in structural organization of the molecular layer, and eventually govern the

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* Morton S. Traum Award Finalist

three-dimensional growth of molecular thin-films, beyond the interface limit. Our research in Berlin aims to provide a molecular scale picture about interactions occurring at the inorganic/organic interface. Our approach to this goal follows a combination of low-temperature scanning tunnelling microscopy and spectroscopy measurements with density functional theory simulations. We characterise the electronic structure of single molecules on a surface with sub-nanometer resolution in order to resolve the influence of local parameters (molecular orientation, neighbourhood, conformation,…) on its properties. Non covalent intermolecular interactions are also relevant at the inorganic interface, and may lead to the construction of three-dimensional supramolecular nanostructures with interesting electronic properties. In this seminar I will present several of our recent results about the electronic configuration of model molecular systems like C60, fullerene-based nanostructures and charge-transfer complexes on metal and semiconductors surfaces. The electronic configuration of the molecular ensembles will be analyzed in terms of their local neighbourhood and the degree of electronic coupling with the metal suface.

10:00am **SS1-FrM7 Reactions of Atomic Hydrogen with Self Assembled Monolayers**, ***J.M. Gorham***, *B. Smith, A. Stover, J.D. Wnuk, H. Fairbrother*, Johns Hopkins University

The interaction of atomic hydrogen with hydrocarbon and semi-fluorinated self assembled monolayers (SAM) has been studied in-situ using x-ray photoelectron spectroscopy (XPS) and ex-situ contact angle measurements. Results indicate that atomic hydrogen (AH) reactions with alkanethiolate SAMs are strongly dependent upon the hydrocarbon chain length. For short chained SAMs (ie. C_9 and C_{12}), AH permeates rapidly through the hydrocarbon film and reacts primarily with the native thiolate bond resulting in chain desorption, as evidenced by a simultaneous loss in both carbon and sulfur. Conversely, sulfur was removed preferentially from longer chained alkanethiolates (ie. C_{16} and C_{18}), followed by the AH mediated erosion of the hydrocarbon film. The different reaction pathways for the long and short chain SAMs are due to effect of chain length on the residence time of AH in the hydrocarbon overlayer. In contrast to the short chain SAMs, AH reactions within the hydrocarbon film become important due to the increased length of the alkyl chain. Reactions of AH with semi-fluorinated SAMs (e.g. $Si\text{-}(CH_2)_2(CF_2)_5(CF_3)$) were consistent with a kinetically controlled process initiated by H atom abstraction from C-H bonds within the SAM. Secondary reactions of the carbon-centered radicals formed in the organic film with AH leads to the desorption of fluorocarbon radicals (e.g. $CF_3(CF_2)_5$). As a result of this reaction mechanism, the rate of fluorocarbon loss from the film is proportional to the adsorbate coverage and the flux of AH. The decrease in contact angle that occurs as a result of AH exposure is directly proportional to the coverage of CF_3 and CF_2 groups, providing a convenient route to control the surface wettability and other interfacial properties. In comparison to low energy electron modification, reactions of AH with semi-fluorinated SAMs are found to be more effective in etching the organic film.

10:20am **SS1-FrM8 Misfit-Dislocation-Mediated Migration of Cu Nanostructures on Ag(111)**, ***A.W. Signor***, *J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have mostly been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to motion of the entire structure, leading to size-independent barriers, and diffusivities that scale with radius according to $D \sim R^{-B}$, with B =1, 2, or 3 for the simplest cases. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a collective mechanism involving glide of misfit dislocations. Here, the entire structure is moved by one Burger's vector b= 1/6 <211> as the dislocation nucleates and glides through the island. Scanning tunneling microscopy (STM) images show that islands with magic sizes have a propensity for defect nucleation and glide leading to enhanced mobility. Quantitative analysis of island trajectories from STM movies collected at 130-200 K yield energy barriers as low as 0.35 eV for this process, even for multilayer islands containing up to ~90 atoms. Significantly, the barriers are very sensitive to island size, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics.

10:40am **SS1-FrM9 Subpicosecond Photodesorption and Photoreaction of CO on Pd(111)**, ***P. Szymanski***, *A.L. Harris, N. Camillone III*, Brookhaven National Laboratory

We have examined the dynamics of the desorption and oxidation of CO on a Pd(111) surface following irradiation with ~110-fs pulses of 780-nm light. For a mixed layer of CO and atomic oxygen, both the desorption of CO and the production of CO_2 exhibit superlinear dependences on the absorbed laser fluence. The fluence dependence of CO desorption at saturation coverage is unaffected by the presence of coadsorbed atomic oxygen. For both CO/Pd(111) and (CO+O)/Pd(111) systems, the probability of CO desorption increases with the initial CO coverage due to population of lower-adsorption-energy sites. Two-pulse correlation (2PC) measurements of the photodesorption yield show rapid relaxation of the excited adsorbate-substrate complex and are well explained by an electron-mediated process. The photoinduced CO_2 production in the (CO+O) mixed layer, by contrast, involves mainly CO molecules with higher binding energies. The 2PC of the CO_2 product is five times broader than that of CO, suggesting that a different effective molecule-surface coupling is responsible for the reaction compared to the desorption. Our results are consistent with a picture where strong coupling between substrate electrons and adsorbed CO leads to high transient adsorbate temperatures, which can cause a subsequent reaction with oxygen if the barrier to direct CO desorption is sufficiently high.

11:00am **SS1-FrM10 Grating-Coupled Excitation of Surface Plasmon Polariton Waves on Single Crystalline Cu(111) using Periodic Density Patterns of Rare Gas Monolayers for Adsorbate Surface Diffusion Study**, ***X.D. Zhu***, *Y.Y. Fei, X. Wang*, University of California at Davis

Using periodic density profiles of xenon (Xe) as thin as 1 ~ 5 monolayers, we have excited and detected grating-coupled surface plasmon polariton waves (SPPW) on Cu(111) in ultrahigh vacuum. The periodic density profiles are formed by laser-induced thermal desorption with a pair of coherent laser pulses at vacuum wavelength of 0.532 microns. The periodicity of the profiles is 5.45 microns. By illuminating the xenon-density-grating-covered Cu(111) with a converging He-Ne laser covering a span of incidence angles from 66.4° to 74.4° and detecting the oblique-incidence reflectivity difference $r_p/r_{p0} - r_s/r_{s0}$ vs. incidence angle with a multiple-element photodiode array, we observed the surface-plasmon resonance (SPR) peaked at the incidence angle of $\theta_{SPR} = 70.4°$ with a full-width at half-maximum of $\Delta_{SPR} = 0.29°$. From the resonance angle θ_{SPR} and Δ_{SPR}, we have determined the optical dielectric constant of single crystalline Cu at 633 nm to be $\varepsilon_{Cu} = -9.53 + i\ 0.142$, markedly different from the literature values for evaporated Cu films. At elevated temperatures such that a xenon density grating on Cu(111) decays in contrast, the surface plasmon resonance as measured by $r_p/r_{p0} - r_s/r_{s0}$ diminishes, reflecting the kinetic of surface diffusion of xenon on Cu(111).

11:20am **SS1-FrM11 Dynamical Study of the Elastic Forces between Dislocations in a Strained Metal Film**, ***B. Diaconescu****, *K. Pohl*, University of New Hampshire

Misfit dislocation networks can be used as natural templates for the growth of 2D large scale ordered arrays of clusters. The strain relaxation in metallic ultra thin films leads to the formation of large scale ordered arrays of dislocations, with unit cell sizes ranging from a few hundred to thousands of atoms. Understanding how the long-range stabilizing forces arrive from atomic interactions will provide a way of controlling the unit cell size and symmetry of the reconstructed surface. Here we show how, using atomically resolved scanning tunneling microscopy data, the dynamical evolution of vibrations of the 2D network of misfit dislocations of atomically thick Ag films on Ru(0001) can provide opportunities for measuring the long range elastic forces that stabilize the system. Fast-scanning STM data at rates of about 3 s/frame are providing a good temporal resolution of the process. In this way, an elastic constant of about 3 $meV/Å^{-2}$ was obtained. The large size of the unit cell does not allow for full ab initio calculations, thus the experimentally determined long range stabilizing forces in such systems are related with first principles interaction parameters via 2D Frenkel-Kontorova models.

Surface Science

Room: 611 - Session SS2+EM+TF-FrM

Organic Films II: Semiconductors and C_{60}

Moderator: J.E. Reutt-Robey, University of Maryland

8:00am **SS2+EM+TF-FrM1 Unravelling Molecular Contrast Formation Obtained by NC-AFM on Titania**, ***R. Bechstein***, *J. Schütte, P. Rahe, A. Kühnle*, University of Osnabrueck, Germany

The (110) surface of TiO_2 constitutes an interesting model substrate for molecular adsorption studies due to its importance in applications such as organic solar cells and light emitting diodes. Several experiments revealed that organic molecules can be anchored to the surface through carboxylic groups both under ultra-high vacuum conditions[1] as well as from solution.[2]

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* Morton S. Traum Award Finalist

We investigated a perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) derivative without carboxylic anchor groups by non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions. The molecules were deposited at room temperature onto TiO$_2$ (110) by evaporation from a Knudsen cell. We achieved true atomic resolution on the bare substrate as well as submolecular resolution on individual molecules. The molecules were observed to align along the [001] direction with the ability to move along this direction. They are found to be homogeneously distributed on the terraces without any tendency to cluster at step edges even at elevated temperature. Two molecular contrast modes are clearly distinguished. In one mode the molecules appear cloudy and are observed to be centred on top of bright rows. In the other mode the molecules are imaged with a dark bone-shaped centre and a bright rim, centred on top of dark rows. Scanning tunnelling microscopy measurements allow to conclude that the molecules are always centred on top of the bridging oxygen rows, demonstrating a contrast reversal between the two NC-AFM imaging modes. By comparing these results with previous NC-AFM studies,[3] we can assign the two modes to positive and negative terminated tips showing that in NC-AFM imaging strongly depends on the tip termination.

[1] A. Sasahara, H. Uetsuka, and H. Onishi, J. Phys. Chem. B 105, 1 (2001)

[2] C. L. Pang, T.-a. Ishibashi, and H. Onishi, Jpn. J. Appl. Phys. 44, 5438 (2005)

[3] J. V. Lauritsen, et al., Nanotechnology 17(14), 3436 (2006).

8:20am **SS2+EM+TF-FrM2 Characterization of Para-Sexiphenyl Thin Films Grown on KCl Substrates**, ***A. Andreev,*** Univ. of Leoben, Austria, *A. Montaigne,* Univ. Linz, Austria, *T. Haber*, Graz Univ. of Tech., Austria, *A. Kadashchuk,* National Academy of Sci. of Ukraine, *G. Hlawacek,* Univ. of Leoben, Austria, *D.-M. Smilgies,* Cornell Univ., *R. Resel, A. Winkler,* Graz Univ. of Tech., Austria, *H. Sitter, N.S. Sariciftci,* Univ. Linz, Austria, *C. Teichert*, Univ. of Leoben, Austria

Para-sexiphenyl (6P) films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work we use Atomic Force Microscopy (AFM), electron microscopy, x-Ray diffraction (XRD), and photoluminescence (PL) in order to find the parameters controlling film morphology, structure, and quality. It is shown that the initial growth stage of 6P on KCl(001) is characterized by the formation of µm-long needles, generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced mounds composed of upright standing molecules developing between the needles are observed and subsequent growth is characterized by a coexistence of both features. It is demonstrated that both features grow directly on the substrate surface, i.e., there is no wetting layer during the deposition of 6P on KCl(001). It is also found that both needles and terraced mounds grown on KCl(001) are single crystalline, in contrast to mica(001), where different oriented 6P domains are formed inside of the chains. PL studies have shown that, as in 6P films on mica, the emission spectra contain two different components - a conventional structured spectrum due to intrinsic excitons and a broad red-shifted band ascribed to some kind of defects. The latter band most clearly can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band was much weaker in the films grown on KCl substrates comparing to that on mica, which corresponds well with results of morphological and structural investigations. This finding confirms the high quality of the films and implies that the defect band is rather sensitive to the structure and morphology of the films. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

8:40am **SS2+EM+TF-FrM3 A Nanoengineering Approach to Regulate The Lateral Heterogeneity of Self-Assembled Monolayers**, *J.-J. Yu, Y.H. Tan, X. Li,* University of California, Davis, *P.K. Kuo,* Wayne State University, ***G.-Y. Liu***, University of California, Davis **INVITED**

Using a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry, regulation of the heterogeneity of self-assembled monolayers (SAMs) is demonstrated. It is known that phase segregated domains would form if SAMs are grown from thiol solutions of mixed compositions. The size and distribution of these domains depend on the interplay between reaction kinetics and dynamics, which can be regulated by varying the reaction conditions including concentration, temperature and reaction time. The reaction mechanism in nanografting, however, differs significantly from self-assembly in the conventional mix-and-grow methods. The spatial confinement in nanografting bypasses the lying-down to standing up transition process, and thus leads to a much fast kinetics. Knowledge of the reaction pathways enables development of methods for shifting the interplay between the kinetics and thermodynamics in SAM formation, and thus the heterogeneity of mixed SAMs. By varying fabrication parameters such as shaving speed, and reaction conditions such as concentration and ratio of the components, the lateral heterogeneity can be adjusted ranging from near molecular mixing to segregated domains of several to tens of nanometers.

9:20am **SS2+EM+TF-FrM5 Mechanistic Aspects of Organic Thin Film Growth from Energetic Sources: Insights from Experiment and Molecular Dynamics Simulations**, ***J.E. Goose***, *A.S. Killampalli, P. Clancy, J.R. Engstrom*, Cornell University

We have used a combination of experiments and molecular dynamics simulations to investigate the fundamental molecular mechanisms contributing to the evolution and final morphology of thin films of pentacene deposited at hyperthermal incident kinetic energies (E_i = 1-10 eV). Experimentally, using supersonic molecular beam scattering techniques and atomic force microscopy we have characterized the adsorption probability as a function of both E_i and the angle of incidence (θ_i). Interestingly, we observe differences in the dynamics of adsorption for pentacene interacting with a clean SiO$_2$ substrate (submonolayer growth) vs. a SiO$_2$ substrate covered by a pentacene thin film (multilayer growth). Specifically, for E_i greater than ~ 1-2 eV, contribution of a new mechanism for pentacene adsorbing on pentacene is implicated. To determine the nature of this mechanism, we have used the non-reactive empirical MM3 potential to model the collision of pentacene molecules with a pentacene thin film using molecular dynamics. Our simulation cell consists of ca. 100 molecules, and includes an upper terrace of 4 x n unit cells, bounded by (010) step edges. Accounting for impacts both near the middle of the terrace and near the step edge, our results from simulation for the probability of adsorption compare very well with those measured experimentally. In particular, adsorption is found to decrease with increasing E_i, and, in general, with increasing θ_i. More importantly, the simulations give us insight into nature of the events that occur at high incident kinetic energies. For thermal incident kinetic energies we observe mostly simple trapping (molecular adsorption), with near unit probability. At higher E_i of 1-5 eV, a significant fraction of molecules (~ 30%) are found to directly insert into the upper terrace, whereas a higher fraction (~ 90%) of molecules impacting near the step edge in this same energy regime also end up incorporating into the upper terrace. Indeed, direct molecular insertion into the pentacene crystal structure is the dominant interlayer process when both the molecule’s orientation and incident angle are aligned normal to the surface, which leads to the formation of interstitials for the time scale of these simulations.

9:40am **SS2+EM+TF-FrM6 Growth of Pentacene Thin Films from a Supersonic Source: Unexpected Behavior in the Presence of Molecular Cluster Formation**, *A. Amassian, S. Hong, S. Bhargava, A.R. Woll, T.W. Schroeder, A.S. Killampalli, J.D. Ferguson, J.D. Brock, G.G. Malliaras,* ***J.R. Engstrom***, Cornell University

We have examined the growth of pentacene thin films on SiO$_2$ using supersonic molecular beam techniques and in situ real-time synchrotron x-ray scattering. At low-to-modest rates of deposition [ca. 0.001 to 0.1 monolayer(ML)/s] we observe an abrupt transition from 2D, layer-by-layer growth to 3D, islanded growth after deposition of the first few monolayers of pentacene on SiO$_2$. At high rates of deposition (ca. 1 ML/s), however, we find persistent 2D crystal growth, and the development of a highly textured film possessing significantly flatter and smoother surface morphology than at low rates of deposition. Concomitantly, in this regime we also observe new polymorphs of pentacene, as significant changes occur in the crystalline structure of the thin films. The transition to this anomalous, yet promising growth behavior corresponds very strongly with the onset of the formation of van der Waals clusters of pentacene within the supersonic expansion. We suggest that the presence of clusters in the incident flux acts to change the dynamics of growth due to a variety of reasons which we discuss. These findings raise the distinct possibility that organic crystals may be synthesized with ultra-flat surface morphology, making them suitable for use in a number of electronics applications where the requirement for abrupt and smooth interfaces has traditionally defaulted to the use of amorphous organic thin films.

10:00am **SS2+EM+TF-FrM7 Vibrational and Structural Investigation of Ferrocene Adsorption on Au(111) Surfaces**, ***G. Pirug***, *M. Kazempoor,* Forschungszentrum Jülich, Germany, *J. Myslivecek,* Charles University in Prague, Czech Republic, *B. Voigtländer*, Forschungszentrum Jülich, Germany

The adsorption of ferrocene (Fe(C$_5$H$_5$)$_2$) on Au(111) surfaces has been studied spectroscopically applying HREELS and XPS as well as structurally by means of LEED and STM under UHV conditions. The vibrational modes observed by HREELS indicate reversible molecular adsorption of ferrocene at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data from solution, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on the sequential appearance and relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from ferrocene molecules with an upright standing molecular axis dominate, as concluded from on- and off-specular HREEL spectra applying the surface dipole selection rules. Dissociation into cyclopentadienyl ring radicals (C_5H_5) can be excluded due to the missing related vibrational losses, such as the wagging mode expected at about 760 cm^{-1}. For multilayer coverages the orientation of the condensed ferrocene molecules is no longer exclusively perpendicular to the surface which results in the appearance of additional vibrational losses. Molecular self assembly yields a well ordered surface structure as shown by topographical STM pictures and LEED pattern.

10:20am **SS2+EM+TF-FrM8 Uncovering Molecular Dewetting: Growth and Morphology of C_{60} and PTCDA on Insulators**, ***S.A. Burke***, *J.M. Mativetsky, S. Fostner, P. Grutter*, McGill University, Canada

Despite considerable interest in recent years in the properties and structural characteristics of molecular deposits for organic based devices, there has been only limited study of growth and morphology of molecular materials on insulating substrates. The majority of traditional surface science tools are significantly hindered by the use of an insulating substrate due to complications with charging and surface damage. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven a powerful surface science tool, and is increasingly being applied to molecular studies on insulators. The power of the technique lies in its ability to image in real-space with sub-angstrom resolution as well as measure structure up to the micron scale allowing for a connection between molecular scale structures and the overall growth morphologies. The nc-AFM technique, operated in UHV, has been applied to two prototypical organic semiconductors: C_{60} and PTCDA, on two well-known insulating surfaces: KBr (001) and NaCl(001). Both systems showed island growth modes with evidence for dewetting, though the resulting morphologies differ considerably. C_{60} on both of these alkali halides forms distinctive branched island shapes. A quantitative analysis of the morphology and its connection to the underlying epitaxy will be discussed. The formation of this branched morphology appears to be a dewetting process which was observed directly in a series of nc-AFM images. The energetics of this system will also be discussed in terms of annealing and deposition onto a heated substrate. PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, monolayer islands are observed in a highly strained c3x3 epitaxy. However, at larger coverages these single layer islands are seen to coexist with tall crystallites exhibiting the same morphology and herringbone structure as observed for PTCDA on KBr, indicating a coverage induced dewetting transition between 0.7 and 0.8 ML. The dewetting was also induced by annealing of the single layer islands yeilding molecular crystals up to several microns long with the familiar herringbone structure of the PTCDA (102) plane. Dewetting has recently been recognized in several other organic systems as a significant factor in the growth and morphology of thin films. The examples presented here may indicate that dewetting is also an important consideration in molecule-on-insulators systems as well.

10:40am **SS2+EM+TF-FrM9 STM/STS Studies of C_{60}:Pentacene Interface Formation**, ***D.B. Dougherty***, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, G. Dutton, J.E. Reutt-Robey*, University of Maryland at College Park, *S.W. Robey*, National Institute of Standards and Technology

The most efficient small-molecule organic solar cells employ heterojunctions between donor and acceptor materials.[1] In order to push the performance of such devices into a regime of cost-effective power generation, it is necessary to develop a detailed understanding of organic-organic interface morphology and its relationship to electronic band alignment. We have approached this question by studying the technologically relevant[2] system of C_{60} deposited onto pentacene, using STM/STS to provide clues to the relative importance of competing intermolecular interactions. When C_{60} is deposited onto a pentacene bilayer on a Ag(111) surface,[3] STM measurements show two unique structures in the first layer. The pentacene bilayer forms a well-ordered structure on Ag(111) with the long molecular axis nearly parallel to the surface. At the lowest coverages, C_{60} forms linear chains whose direction is templated by the underlying pentacene rows, with C_{60} molecules located between rows of pentacene molecules. The details of the observed structural arrangement are related to electrostatic interactions between C_{60} and the pentacene bilayer structure. Information on local relative band alignment for these structures is measured using constant-current distance-voltage spectroscopy.[4] The local transport gap for C_{60} linear chains is 4.4±0.2 eV compared with a gap of 3.7±0.2 eV for the surrounding pentacene bilayer. The magnitudes of the gaps are influenced by local polarization energies in each structure. At higher coverage, domains of C_{60} with no discernable long range order dominate the first layer. This disorder probably arises from frustrated intermolecular interactions between the two different chemical species. The lateral interactions between C_{60} molecules (favoring hexagonal ordering) cannot be optimized simultaneously with the comparable strength interactions between C_{60} and the underlying pentacene film (favoring an oblique unit cell). *This work has been partially supported by the Dept. of Commerce through the NIST Center of Nanomanufacturing and Metrology and the NSF-funded MRSEC via DMR-05-20471.

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[3] Eremtchenko et al., Phys. Rev. B 72, 115430 (2005).

[4] S.F. Alvarado, et al., Phys. Rev. Lett. 81, 1082 (1998).

11:00am **SS2+EM+TF-FrM10 Potassium Induced Long Range Superstructure on C_{60}/Ag (111) Surface**, *C.-C. Kuo, **W.W. Pai***, National Taiwan University

Various long range superstructures were observed for potassium (K) doped C_{60} monolayer on Ag (111) by scanning tunnelling microscopy (STM). Pristine C_{60} monolayer exhibits a bright-dim contrast in the most stable $(2\sqrt{3}\times2\sqrt{3})$-R30 phase, whereas the molecular contrast is uniform in other metastable phases (denoted as R12 or R48 phases). Upon K doping, K segregate into compact islands at room temperature and the bright-dim contrast in the R30 phase is eliminated. Furthermore, ordered quasi-hexagonal patterns with periodicities of ~7 nm to ~40 nm appear. The ordered superstructures show distinct characteristics in each C_{60} phase. Close inspection reveals that the super lattices are not exactly hexagonal but exhibit uni-directional distortion. Therefore, the finding is perplexing as it cannot be explained by, e.g., Morie patterns. We propose that the superstructures are due to overlaying an orthorhombic one-dimensional polymerized KC_{60} phase over the hexagonal silver lattice. This is supported by high-resolution STM images showing the signature of [2+2] covalent bond formation.

11:20am **SS2+EM+TF-FrM11 Thiol-Modified Diamondoid Monolayers on Silver and Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, Lawrence Livermore National Lab., *J.D. Fabbri*, Stanford Univ., *J.R.I. Lee*, Lawrence Livermore National Lab., *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *J.E. Dahl, R.M.K. Carlson, S.G. Liu*, MolecularDiamond Tech., *T. van Buuren*, Lawrence Livermore National Lab., *N.A. Melosh*, Stanford Univ.

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have negative electron affinity, a desirable property for electron emission. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to absorb on gold with high coverage. The availability of diamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency electron emitters, as well as crystals for diamond growth or other nanotechnological applications, and fundamental studies of the electronic and structural properties of these molecular monolayers are a necessary precursor. We have investigated the effects of thiol substitution position, polymantane order, and metal substrate on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon these parameters. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

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