# Monday Morning, November 13, 2006

## Surface Science
## Room 2002 - Session SS1-MoM

### Catalytic Chemistry of Hydrocarbons
**Moderator:** J.N. Andersen, Lund University, Sweden

**8:00am SS1-MoM1 Activation of Au for Nitrogen Addition Reactions**, *X. Deng, T.A. Baker, C.M. Friend,* Harvard University
Aziridination, nitrilation and hydrogenation of styrene are promoted on Au(111) pre-covered with NHx groups. NH, N and H were formed on Au(111) at 110 K by electron bombardment of condensed ammonia. 2-phenylaziridine is the major product, accounting for 63% of the total styrene conversion; it is attributed to the addition of NH to styrene. In addition, benzonitrile, benzyl nitrile and ethylbenzene are produced due to reactions with adsorbed N and H atoms, respectively. These observations establish a clear guide for the possible application of supported Au catalysts in the future.

**8:20am SS1-MoM2 Toward Computational Screening in Heterogeneous Catalysis: Pareto-Optimal Methanation Catalysts**, *M.P. Andersson,* Technical University of Denmark, Denmark*; T. Bligaard, A. Kustov, K.E. Larsen, J. Greeley, T. Johannessen, C.H. Christensen,* Technical University of Denmark*; J.K. Norskov,* Technical University of Denmark, Denmark
In this work we make the first step towards a computational screening for catalyst materials based on density functional theory and apply it to find new metal alloy materials for the methanation reaction (CO + 3H@sub 2@ -> CH@sub 4@ + H@sub 2@O), see e.g.@footnote 1@ We do so by using the following procedure: First we establish a descriptor for the reaction, which we then use to screen new alloy materials for high activity. The most interesting candidates are investigated in more detail using density functional theory and their methanation activities are finally tested experimentally. The descriptor is chosen based on the fact that there are two key parameters for methanation: The CO dissociation barrier and the stability of the intermediates C and O. These two properties are furthermore linearly related in a so-called Brønsted-Evans-Polanyi (BEP) relation@footnote 3@ and we are able to reduce them to a single descriptor, the dissociation energy of CO, which gives the expected volcano shaped curve. We have screened 117 binary alloys by estimating activity and price from interpolation of the bulk composition. We make a simultaneous optimization of both activity and price via a pareto plot,@footnote 2@ and we predict FeNi and FeNi@sub 3@ alloys to be both more active and cheaper than pure Ni catalysts (the current industrial catalysts). Full density functional theory calculations confirm the results of the interpolation scheme. Finally we have investigated the activity towards methanation for Fe-Ni alloys and have found that alloys with 50-75% Ni have an activity better thatn pure Ni by about a factor of two to three. @FootnoteText@ @footnote 1@Sehested J, Dahl S, Jacobsen J, et.al. J. Phys. Chem. B 109, 2432-2438 (2005)@footnote 2@Bligaard T, Johannesson GH, Ruban AV, et.al. Appl. Phys. Lett. 83, 4527-4529 (2003).@footnote 3@Nørskov JK, Bligaard T, Logadottir A. et.al. J. Catal. 209, 275-278 (2002).

**8:40am SS1-MoM3 Double-Bond Isomerization in Cyclic Olefins Adsorbed on Platinum Surfaces.**, *R. Morales, F. Zaera,* University of California, Riverside
The migration & cis-trans isomerization of C=C in olefins is central to many processes in oil refining and food processing.It has been well established that those reactions follow simple half hydrog. and dehydrog. steps according to the Horiuti-Polanyi mech.,but that still leaves a number of subtle issues associated with the stereo- & regiospecificity of the reactions involved.For instance,the branched alkyls that may form as intermediates after half hydrog. of substituted olefins may have beta-H in diff. environments,and elimination of those in the step that regenerates the olefin may lead to diff. products.Here we show that this is certainly the case with methyl cyclopentenes & methyl cyclohexenes,where the C=C may be in either exo and endo positions.We have studied the chemistry of those compounds on Pt(111) single-crystal surfaces under UHV by means of TPD & RAIRS.Those molecules were chosen because of the particular lability of their allylic H,and because they may offer significance hindrance towards normal olefin adsorp. and alkyl-alkene interconversion reactions.It was found that both the C5- and C6-cyclic molecules undergo dehydrog. in a stepwise manner,but with different kinetics depending on the position of the C=C.For instance,while methylene cycloalkanes decompose in four dehydrogenation stages,1-methyl-1-cycloalkenes display only three distinct decomposition stages.Also,the molecules with internal C=C proved more stable than those with the unsaturation in the external position,a fact that facilitates the hydrog. of methylene-C5 and methylene-C6 to the corresponding cycloalkanes and their isomerization to 1MC5= and 1MC6=,resp.In addition,it was shown that aromatization reactions,to form benzene or toluene,can be driven at higher temps.It was determined by using RAIRS that ring expansion for the 1MC5= and methylene cyclopentane does not take place via an allylic intermediate,but by the formation of a methylcyclopentadiene species instead.

**9:20am SS1-MoM5 Catalysis Science of Surface Metal Oxide Catalytic Active Sites**, *I.E. Wachs,* Lehigh University **INVITED**
Surface metal oxide sites represent the catalytic active sites present in oxide-based catalytic materials(zeolites, supported metal oxides, heteropolyoxo anions, bulk mixed metal oxides and clays). Recent in situ and operando Raman, IR and UV-Vis DRS characterization advances are allowing for the complete determination of the molecular and electronic structures of the surface metal oxide catalytic active surface sites under reaction conditions. Combination of the molecular and electronic structural information with the corresponding kinetics of the surface chemistry is allowing, for the first time, the establishment of molecular/electronic structure-activity/selectivity relationships. These fundamental studies with molecularly designed metal oxide catalysts are allowing for the direct determination of the number of catalytic active sites involved in a specific catalytic reaction (one, two or greater), the relative contributions of isolated and polymeric surface metal oxide sites as well as oxide nanoparticles, the role of the oxide support ligand, the effect of cation oxidation state, and the mechanism by which promoters influence specific catalytic reactions.

**10:20am SS1-MoM8 Methanethiol Desulfurization on Titania-Supported Ni Clusters**, *O. Ozturk, J.B. Park, D.A. Chen,* University of South Carolina
The hydrodesulfurization chemistry of methanethiol has been studied on Ni clusters supported on TiO@sub 2@(110). Ni clusters of different sizes and with uniform size distributions have been deposited on the titania substrate and characterized by scanning tunneling microscopy (STM). After heating methanethiol adsorbed on the Ni clusters to various temperatures, high resolution X-ray photoelectron spectroscopy (XPS) studies demonstrate that methyl thiolate is formed as a surface intermediate, and atomic sulfur remains on the surface after methyl thiolate decomposition. Furthermore, the S(2p) binding energies suggest that the surfaces of the Ni clusters have predominantly (110) structure. Temperature programmed desorption (TPD) experiments show that methane and hydrogen are the major gaseous products formed from methanethiol decomposition on Ni clusters of all sizes, and CO is also formed a minor product via oxidation of atomic carbon by lattice oxygen. Both XPS and TPD studies indicate that the larger, annealed Ni clusters have decreased activity compared to the smaller clusters deposited at room temperature; this loss of activity may be related to partial encapsulation of the Ni clusters by TiO@sub x@ upon heating.

**10:40am SS1-MoM9 Chiral Surface Structure and Enantioselectivity**, *A.J. Gellman,* Carnegie Mellon University*; J.D. Horvath,* Milliken Corp.*; Y. Huang,* Carnegie Mellon University*; A. Koritnik,* University of Michigan
High Miller index metal surfaces with structures lacking mirror symmetry are naturally chiral and have enantiospecific interactions with chiral adsorbates. This set of surfaces spans the interior of the stereographic projection of surface structures. In the case of fcc lattices the chiral surfaces are those that have kink-step-terrace structures. The adsorption of R-3-methylcyclohexanone is enantiospecific in the sense that its desorption energies from the chiral kinks are dependent on the handedness of the kink. The kinks, steps and terraces on the high Miller index surfaces are formed by the (100), (110) and (111) microfacets. Thus there are, in principle, only six types of kinked surfaces dictated by which of the three microfacets forms the kink, step and terrace. R-3-methylcyclohexanone adsorption and temperature programmed desorption has been studied on a set of 9 achiral Cu surfaces and on both the R- and S-enantiomers of a set of 7 chiral Cu surfaces. Six of the chiral surfaces have been chosen to fall within the six zones of the stereographic projection having surface structures formed of the six combinations of kink, step and terrace formed by (100), (110) and (111) microfacets. The desorption spectra of R-3-methylcyclohexanone can be resolved into components arising from desorption from the kinks, the step edges and form the terraces of each of the surfaces. The desorption from the kink sites is enantiospecific in the sense that the R-3-methylcyclohexanone has different desorption energies from the two enantiomers of the surfaces. The enantiospecificity of the

desorption energies varies from @DELTA@@DELTA@E@sub des@ = 0.2 to 1.0 kJ/mole.

**11:00am SS1-MoM10 Diffusion of Adsorbates: on "Walking" and "Dancing" Molecules**, *K.-Y. Kwon, K.L. Wong, G. Pawin, X. Lin, R. Frisbee,* **L. Bartels**, University of California at Riverside **INVITED**
We report on the diffusion of individual 9,10-dithioanthracene (DTA) and CO molecules on Cu(111). DTA adsorbs with the aromatic backbone lying flat on the substrate and with both sulfur atoms attached to it. In variable-temperature STM studies, we find that DTA possesses the notable property, that it diffuses exclusive in the direction of its aromatic ring system. It achieves this by moving its substrate linkers in an alternating fashion much resembling bipedal locomotion. Over a wide temperature range we neither find rotation of the molecule in the surface plane nor diffusion perpendicular to the aromatic system. Consequently, an individual molecule is confined to shuttle forward and backward along a straight line albeit the sixfold symmetry of the top substrate layer. We will discuss possible extensions of this work towards breaking of the forward/backward symmetry, transport, etc. DTA forms molecular rows rather than islands on Cu(111). Exchange of the thiol linkers by carbonyl causes these rows to form a mesh resembling a honeycomb with regular "pore" sizes of ca. 50 Angstrom, much larger than the molecule itself. We contrast the behavior of DTA with that of CO on the same surface: CO diffusion was found to be generally isotropic, as expected, and depending on the local coverage. At a local coverage corresponding to one molecule per 20 substrate atoms, CO has a 3 times higher diffusion rate than an isolated molecule. The diffusion barrier for isolated CO molecules was found to be 75 Â± 5 meV at a prefactor of 10 MHz. Time-lapsed STM measurements provide 2D trajectories of the motion of CO molecules and pairs of them. The latter exhibit dominantly tangential diffusion at close CO-CO proximity Taking into account the diffusion directions as well as the intermolecular distances, the 2D diffusion potential of a CO in the vicinity of another CO can be reconstructed.

**11:40am SS1-MoM12 Comparison of the Stability of Small Molecules On Rh(111) and Rh(553)**, *A. Resta, J. Gustafson, R. Westerström, E. Lundgren, A. Mikkelsen, J.N. Andersen,* Lund University, Sweden
We have studied the adsorption and thermally induced reactions of C@sub 2@H@sub 4@ and C@sub 2@H@sub 5@OH, on Rh(111) and Rh(553) with particular emphasis on the differences induced by the atomic steps present on the vicinal Rh(553) surface. The development of surface species was followed at temperatures ranging from 100 K to 680 K by chemically sensitive high resolution core level photoemission (HRCLS) applied to the adsorbate C1s and O1s and the substrate Rh 3d levels. Comparing results from the two surfaces, we find a number of differences which can be ascribed to reactions occurring in the vicinity of the steps on Rh(553). For C@sub 2@H@sub 4@ we monitor the formation and subsequent decomposition of ethylidyne (CCH@sub 3@) by saturating the surfaces with C@sub 2@H@sub 4@ at 100K followed by annealing at increasingly higher temperatures. We find that both the formation as well as the decomposition of ethylidyne occur at a lower temperature on Rh(553) than on Rh(111). Although HRCLS spectra indicate similar decomposition products on both surfaces, a more detailed analysis suggests significantly different decomposition scenarios on the two surfaces. In similar annealing experiments of a few layers of C@sub 2@H@sub 5@OH we find that the formation of CO, which indicates the breaking of the C-C bond in ethanol, occurs at lower temperature on Rh(553) than on Rh(111). We never observe atomic O or OH-like groups on neither surface. In addition to the temperature differences we also find significantly different fragmentation patterns on the two surfaces. For instance, ethylidyne is shown to form on Rh(111) but is absent from Rh(553).

## Surface Science
## Room 2004 - Session SS2-MoM

### Gas-Surface Reaction Dynamics
**Moderator:** P.D. Johnson, Brookhaven National Laboratory

**8:00am SS2-MoM1 Biphasic Substrate-Adsorbate Energy Transfer Following Subpicosecond Photoexcitation**, *P. Szymanski, A.L. Harris, M.G. White,* Brookhaven National Laboratory; **N. Camillone III,** Brookhaven National Laboratory, Suffolk
Photodesorption of carbon monoxide molecules from a Pd(111) surface caused by femtosecond laser pulses was studied by two-pulse correlation measurements. The measured decay of the desorption yield with pump-probe delay reveals that the dynamics of energy transfer are independent of surface coverage and are biphasic, comprising two components with subpicosecond and 30-ps characteristic decay times. The relative contribution of the slower component to the total desorption yield is found to decrease as the difference between the desorption temperature and the surface temperature increases. This behavior is consistent with simultaneous excitation coupling from both electrons and phonons of the metal into the adsorbate-substrate bond. The strong contributions from two separate coupling mechanisms is distinct from that observed for CO desorption from other metals (e.g., Cu and Ru), where either fast or slow coupling predominates.

**8:20am SS2-MoM2 Influence of Film Thickness on the Reactions of Gas Phase Radicals with Self Assembled Monolayers**, *H. Fairbrother, J. Gorham,* Johns Hopkins University
The influence of chain length in the reactions of thin film assemblies with reactive gas phase species has been identified in studies designed to probe the modification of alkanethiolates by atomic hydrogen (AH). In these studies the change in chemical composition of four alkanethiolate self assembled monolayers (SAMs), octadecanethiolate, hexadecanethiolate, dodecanethiolate and nonathiolate, as a result of exposure to atomic hydrogen have been studied in situ, using X-ray Photoelectron Spectroscopy. Reactions of atomic hydrogen with the native thiolate S atoms at the film/substrate interface are responsible for sulfur desorption and the formation of new C-S-C species. For each alkanethiolate, exposure to atomic hydrogen results in a loss of sulfur and carbon. The rate of sulfur loss from each SAM are well described by first order kinetics with a rate constant that increases with increasing chain length. This is consistent with the idea that sulfur desorption is controlled by the rate of atomic hydrogen permeation through the hydrocarbon overlayer. In the two shorter chain SAMs, the initial loss of carbon and sulfur is strongly correlated, indicative of a dominant role for the desorption of intact adsorbate chains and large alkyl sulfur fragments. In contrast, for octadecanethiolate and hexadecanethiolate SAMs the rate of carbon loss is dramatically reduced and the carbon and sulfur desorption kinetics are uncorrelated. In these longer chain SAMs the variation in the filmâ?Ts chemical composition as a function of AH exposure is consistent with the formation of a disordered carbonaceous overlayer, due to cross-linking reactions between adjacent hydrocarbon chains, before atomic hydrogen permeates to the film/substrate interface. Results from this investigation highlight the important role that film thickness can play in moderating the reaction kinetics in organized thin film assemblies.

**8:40am SS2-MoM3 Activated Dissociative Chemisorption: Distinguishing Between Statistical and Dynamical Behavior**, *I. Harrison,* University of Virginia **INVITED**
Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple, two to three parameter, microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this "nonequilibrium gap" for several activated dissociative chemisorption reactions [e.g., H@sub2@ on Cu(111); CH@sub4@ on Ni(100), Pt(111), Ir(111), and Ru(0001); SiH@sub4@ on Si(100); and C@sub2@H@sub6@ on Pt(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces. Identification of the essential role of surface phonons and the approximate spectator status of rotational motion in the H@sub2@ dissociation dynamics on Cu(111) will be highlighted in this talk.

**9:40am SS2-MoM6 Vibrational Energy Flow in a Gas-Surface Reaction**, *D.R. Killelea[1], A.L. Utz,* Tufts University
Energy flow plays a central role in the activation of surface reactions. We measure how energy selectively deposited into the translational, rotational, and translational coordinates of methane influences S@sub 0@ on Ni(100) and Ni(111) to answer key questions about energy flow in this prototypical gas-surface reaction. Infrared laser excitation of CH@sub 4@ in a supersonic molecular beam prepares a microcanonical ensemble of reagents with well-defined internal and translational energies. We quantify

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

reactivity for the state-selected reagents and observe non-statistical patterns of activation, including vibrational mode specificity. For example, the @nu@@sub 3@ C-H stretch is more reactive than the second overtone of the umbrella-bending mode, 3@nu@@sub 4@, even though 3@nu@@sub 4@ contains 30% more energy. On Ni(111) energy deposited in @nu@@sub 3@ activates dissociative chemisorption more than an equivalent amount of translational energy. To understand these results, we propose a framework for describing energy flow among the energetic degrees of freedom available to the molecule-surface reaction complex. Our model draws on and is consistent with descriptions of intramolecular vibrational energy flow in both the gas-phase and in liquids, but accounts for features unique to gas-surface reactivity. We focus on the characteristic timescales for energy flow and the molecule-surface interaction time. We conclude that for direct dissociative chemisorption of CH@sub 4@, there is insufficient time for full energy randomization among the energetic degrees of freedom in the molecule-surface reaction complex. Our model not only predicts vibrational mode-specific behavior - it also suggests a consistent explanation of surface temperature effects, explains the success of statistical theories to model ensemble-averaged reactivity even when energy flow is not statistical, and provides a framework for assessing the extent of energy flow in other gas-surface reactions.

**10:20am SS2-MoM8 Ultrafast Structural Dynamics in Complex Materials using Femtosecond Visible and X-ray Pulses**, *R.W. Schoenlein,* Lawrence Berkeley National Laboratory                                    **INVITED**
Understanding the correlated interplay between atomic structure and electronic structure and properties is a fundamental challenge in condensed matter physics, particularly for correlated materials exhibiting strong coupling between charge, spin, orbit, and lattice vibrational degrees of freedom. Time-resolved measurements provide a new window to this problem by enabling the study of coupled interactions on time scales shorter than the underlying correlations. This talk will focus on recent ultrafast measurements of photo-induced phase transitions in transition-metal oxides, molecular complexes, and manganites in which the underlying mechanism of the phase transition is revealed by the time-scale of the dynamics. The talk will also discuss recent progress in the development and application of ultrafast x-ray techniques to the study of atomic and electronic structural dynamics in complex materials. X-rays are ideal probes of atomic structure, and offer important advantages for probing electronic structure as well (valence states, bonding geometry etc.) The application of x-ray structural probes on the time scale of a vibrational period, ~100 fs, is an important new tool for understanding complex materials.

**11:00am SS2-MoM10 Direct Probing of the Surface Dangling Bond by Means of Evanescent Wave Cavity Ring Down Spectroscopy**, *M.C.M. Van De Sanden, I.M.P. Aarts,* Eindhoven University of Technology, The Netherlands*; A.C.R. Pipino,* NIST*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands
The surface interaction of gas phase species plays an important role in crystal and thin film growth, chemical passivation and heterogeneous catalysis. Adsorbants, with usually a significant coverage, can be measured using scanning probe, optical or nuclear techniques, preferably in situ and real time. The surface kinetics however, are usually controlled through the creation of a so-called dangling bond. In this contribution we demonstrate a novel technique to probe surface dangling bonds directly and in real time. The method employed is based on evanescent wave cavity ring down absorption spectroscopy using an ultralow-loss fused silica monolithic folded resonator.@footnote 1@ On the curved surface of the folded resonator a thin hydrogenated amorphous silicon (~800 nm) is grown by means of hot wire assisted chemical vapor deposition. The broad band absorption feature of the dangling bond is probed between 1170 and 1245 nm with an unprecedented sensitivity. Absorption losses as low as 10@super -7@ per laser pulse can be measured, corresponding with a surface dangling bond coverage of 10@super -6@! The a-Si:H film was dosed using a calibrated atomic hydrogen. Uptake curves were measured as function of atomic hydrogen flux. The saturated surface coverage measured was around 5 10@super -4@ for an H-flux of 2 10@super 14@ cm@super -2@@super-1@ at a measured abstraction probability from the initial up-take curves of around 0.01±0.003. These results, which confirm previous reports on H saturated surfaces, might point towards a hot-precursor related adsorption-desorption mechanism. However we clearly observe a saturated surface coverage that is H-flux dependent, in contrast with predictions based on Langmuir-Hinshelwood or Eley-Rideal mechanism. In addition we report on the self passivating effect of a-Si:H

surfaces after the dosing with atomic hydrogen has ended. @FootnoteText@ @footnote 1@ Aarts et al. PRL 95 166104 (2005).

**11:20am SS2-MoM11 Image and Image-Derived States Formed by Molecular Thin Film Structures**, *E.T. Jensen,* University of Northern B.C., Canada*; L. Sanche,* Universite de Sherbrooke, Canada
Electron transport through and interaction with molecular thin films is an area of much current interest. In this work, electron image states formed at molecular interfaces have been used to enhance the trapping of low energy electrons by adsorbed 'detector' molecules.@footnote 1@ A magnetically collimated low energy electron beam (electron energies between 0 and 10eV) is incident upon prepared molecular thin films, and the formation of stable anions at the surface are monitored using a charge trapping technique.@footnote 2@ We have studied thin films prepared on a cold (T=15K) polycrystalline platinum substrate. Molecular films are grown on top of a 10ML thick Kr spacer layer, to isolate the film from the metal substrate. On this Kr/Pt substrate we have grown various thin molecular films (1-10ML thick) that support image states. We have studied image states formed at the surface of methanol, 1-butanol, n-octane and difluoromethane thin films. Low energy electron transmission spectra show that all these films display a conduction band gap near the vacuum level, which is crucial in supporting long-lived image states. To detect the image states formed by these molecular thin films, we introduce submonolayer quantities of 'detector' molecules that can be dissociated by low energy electrons to create stable anions (CH@sub 3@I, CH@sub 3@Br, CH@sub 3@Cl) or which support stable molecular anions (CO@sub 2@). We have studied image state enhanced electron trapping at the molecular film-vacuum interface. We have also created and studied molecular film 'quantum well' type structures in which the detector molecules are placed in a Kr spacer between two molecular thin films- in the region between two films an image-state derived quantum well state can be identified. @FootnoteText@ @footnote 1@ K. Nagesha and L. Sanche, Phys. Rev. Lett. 81, (1998) 5892.@footnote 2@ K. Nagesha, J. Gamache, A.D. Bass and L. Sanche, Rev. Sci. Inst. 68, (1997) 3883.

**11:40am SS2-MoM12 Reaction Dynamics of NO Gas on Iron Phthalocyanine Thin Films**, *N.L. Tran,* University of California at San Diego, Unites States*; S.R. Bishop, G.C. Poon, A.C. Kummel,* University of California at San Diego
Metallophthalocyanines (MPcs) have been proposed for use in organic-based chemical field effect transistor (chem-FET) detectors for the measurement of ambient gases such as NO@sub x@, NH@sub 3@ and O@sub 3@. However, the mechanisms of the reaction between these gases and MPc thin films have not been studied. We have investigated the reaction dynamics between NO gas and a monolayer iron phthalocyanine (FePc) on a Au(111) substrate. Sticking probabilities of a molecular beam of NO were measured on both clean Au(111) and ordered monolayer FePc deposited on clean Au(111). The sticking probabilities were measured both as a function of beam energy (0.09eV - 0.4eV) and surface temperature (125K - 325K). The sticking probability of NO onto the FePc film saturates at 3% of a ML for all surface temperatures and all incident kinetic energies consistent with the final chemisorption site being confined to the FePc metal center. In contrast to the saturation coverage, the sticking probability is large (40%) at low surface temperature and low incident kinetic energy and decreases linearly with increasing surface temperature but is independent of beam energy above 0.26eV. Temperature dependent sticking which is independent of kinetic energy is not consistent with simple models of direct chemisorption nor precursor mediated chemisorption. Instead, the data is consistent with NO sticking onto the monolayer FePc via multiple precursor-mediated physisorption pathways in which the NO traps onto the aromatic rings and then diffuses to the metal center on FePc. Density functional theory simulations of NO binding onto the FePc molecule also support this theory. These calculations show a multi-step absorption mechanism in which NO initially binds to the inner ring nitrogens and subsequently migrates to the deep chemisorption well on the metal centers for FePc.

## Surface Science
## Room 2002 - Session SS1-MoA

### Catalysis for the Hydrogen Economy
Moderator: G. Fisher, Delphi Research Labs

**2:00pm SS1-MoA1 Catalytic Hydrogen Production**, *J.K. Norskov,* Technical University of Denmark, Denmark*; **J. Greeley,*** Technical University of Denmark **INVITED**
The possibility of using molecular hydrogen as a fuel focuses attention on the way it is produced. Methods include catalytic conversion of hydrocarbons and electrochemical or photochemical water splitting. Certain enzymes, hydrogenases and nitrogenases, catalyze hydrogen evolution. Attempts at using density functional theory calculations to understand both the inorganic and biological catalysts will be described. It will also be shown how the insight may be used to identify new catalysts in this area.

**2:40pm SS1-MoA3 Hydrogen Production from Ethanol Over Bimetallic Catalysts**, *P.Y. Sheng, A. Yee, W. Chiu, **H. Idriss,*** University of Auckland, New Zealand
Hydrogen is one of the most plausible alternative energy sources that can be widely used in the near future if sustainable ways of generating it are found. This work focuses on the reactions of ethanol, as an example of a bio-fuel, on the surfaces of platinum, palladium and rhodium supported on ceria (of size 10 to 20 nm). The bimetallic compounds: Pt-Rh, Rh-Pd, and Pt-Pd were also investigated. The addition of any of the above metals to CeO@sub2@ was found to suppress the oxidation of ethanol to acetates at room temperature, as there are fewer surface oxygen atoms available to oxidize the ethanol (the remaining oxygen atoms did not produce efficient oxidation). Ethanol dehydrogenation to acetaldehyde was facilitated by the presence of Pt or Pd; at higher temperatures the acetaldehyde condensed to other organic compounds, such as crotonaldehyde. By contrast, in the presence of Rh only traces of acetaldehyde or other organic compounds were seen on the surface, and detectable amounts of CO were found upon ethanol adsorption at room temperature. This indicates the powerful nature of Rh in breaking the carbon-carbon bond in ethanol. The effects of prior reduction were also investigated and clear differences were seen: for example, a shift in reaction selectivity is observed for the bimetallic Rh-containing catalysts. Methane was the dominant hydrocarbon on the reduced catalysts while acetaldehyde was the main product for the non-reduced ones. Hydrogen formation was monitored during steady state ethanol oxidation and Pt-Rh and Rh-Au were found to be the most active catalysts.

**3:00pm SS1-MoA4 Design and Stability of Surface Alloys used for Catalytic Conversion of Fossil Fuel to Hydrogen**, *J. Knudsen*[1]*, R.T. Vang,* University of Aarhus, Denmark*; J. Schnadt,* University of Aarhus, Denmark, Sweden*; E.K. Vestergaard, T.M. Pedersen, B. Hammer, T. An, I. Stensgaard, E. Laegsgaard,* University of Aarhus, Denmark*; A.U. Nilekar, M. Mavrikakis,* University of Wisconsin-Madison*; F. Besenbacher,* University of Aarhus, Denmark
Clean, cheap and efficient production of high-purity hydrogen is an essential prerequisite for the emerging hydrogen economy. The vast majority of the present hydrogen production comes from catalytic conversion of fossil fuel, which relies heavily on the steam reforming (SR) reaction and the Water-Gas-Shift (WGS) reaction. Supported Ni particles are commercially used as catalysts for the SR reaction, whereas supported Cu particles are currently used for the low-temperature WGS reaction. In this study vacuum deposition of Cu onto Pt(111) at 800 K is used to synthesize stable near-surface alloys (NSA) of Cu/Pt(111). A combination of scanning tunneling microscopy (STM), Core-level photoemission (XPS), Thermal desorption spectroscopy (TDS) and Density functional theory (DFT) is used to characterize the NSAs, and it is found that Cu atoms are stabilized sub-surface, leaving a surface layer free of Cu atoms. Very interestingly, we find that the WGS activity of our new NSA is superior to that of Cu(111), and it is, therefore, very likely that real Cu/Pt near-surface particles could be used as new and improved catalysts for the WGS reaction. Finally, fast high-pressure STM experiments in a high CO pressure are used to examine the stability of this new Cu/Pt(111) near-surface alloy for the WGS reaction, and a previously found Au/Ni(111) surface alloy, which can be used for the SR reaction. From these experiments we conclude that the Cu/Pt(111) NSA remains stable in high pressure of CO in contrast to the Au/Ni(111) surface alloy, which is found to phase separate into small Au clusters on a Ni(111) substrate due to formation of Ni-carbonyls, which remove Ni from the surface.

**3:20pm SS1-MoA5 Thermodynamic Investigations into the Redox Properties of Mixed-Oxide Catalysts Relevant to Hydrogen Production**, *R.J. Gorte,* University of Pennsylvania **INVITED**
Many of the reactions for hydrocarbon reforming, including steam reforming and water-gas shift, can be thought of as redox reactions. It is therefore not surprising that catalytic activities can be enhanced significantly by including a redox catalyst, such as ceria. In most cases, the redox catalysts are in the form of a mixed oxide, such as ceria-zirconia, and the thermodynamic properties for oxidation and reduction of these mixed oxides are usually not known. In this talk, I will discuss our investigations into the redox properties of selected materials, including solid solutions of ceria and zirconia. Reduction isotherms were determined over a temperature range using TPR methods and Coulomb Titration. For ceria-zirconia, the thermodynamic properties were found to be a strong function of composition but were independent of sample surface area and calcination temperature, so long as the oxide structure was maintained. While the enthalpy of reduction for ceria-zirconia solutions is less than that of pure ceria, at least some of the interesting properties of this material are associated with entropy effects.

**4:20pm SS1-MoA8 Electrode Catalysts of Polymer Electrolyte Fuel Cell using Carbon Nanotube**, *J. Nakamura, E. Yoo, T. Watanabe,* University of Tsukuba, Japan
The high-priced and limited Pt constitutes a high barrier to commercialization of fuel cells. Pt is essential for the electrode catalyst of polymer electrolyte fuel cells (PEFCs). Reduction in Pt usage is one of the key requirements for the commercialization of fuel cells 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. This is due to efficient formation of triple phase boundary (electrode/electrolyte/gas). Recently, we observed that Ru/Pt/CNT shows higher tolerance for CO poisoning compared to Ru/Pt/carbon black. This suggests that the interface between carbon and alloy catalysts is very different so that the Ru-Pt alloy phase is modified in terms of catalytic nature. The shape of metal catalyst particles is elongated on CNT surfaces, while catalysts on carbon black or defected carbon surfaces is spherical. This is the consequence of the difference in the state of the interface. In general, the electric double layer is formed at the interface between metallic surfaces, where electrons flow from materials with low work function to those with high work function. The electric double layer causes attractive interaction at the interface. The observed support effect of CNT is ascribed to the strong interaction between flat graphene sheet and Pt-Ru alloy particles, leading to the modification of catalytic nature. In this presentation, we report and discuss the effect of carbon surface below metal catalysts upon the performance of electrode catalysts by showing the results of CNT supported electrode catalysts and model system of metal catalysts/HOPG (Highly oriented pyrolytic graphite).

**4:40pm SS1-MoA9 Effect of Hydrogen on the Stability of Ti on an Al Surface\***, *R. Bastasz,* Sandia National Laboratories*; W.P. Ellis,* Los Alamos National Laboratory*; R. Stumpf, J.A. Whaley,* Sandia National Laboratories
The thermal stability of Ti atoms evaporated onto an Al(100) surface was studied using the surface-sensitive technique of ion scattering spectroscopy (ISS). Measurements were made in vacuum and in the presence of an atomic deuterium beam directed at the sample. When heated in vacuum, Ti begins to disappear from the surface at substrate temperatures below 100°C and is completely absent at temperatures above 250°C. When a similar measurement is made while the sample is being exposed to a flux of deuterium atoms, the Ti persists on the surface to noticeably higher temperatures. Diffusion coefficients for Ti into Al were obtained from ISS data in both cases at selected substrate temperatures in the range 50-150°C. The activation energy for diffusion of Ti from the Al(100) surface appeared to be altered in the presence of D. The experimental results are interpreted using density functional theory, which indicates that H-Ti interactions stabilize surface Ti. @FootnoteText@ *This work was supported by the US Dept. of Energy under contract DE-AC04-94AL85000.

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

## Surface Science
## Room 2004 - Session SS2-MoA

### Functionalization of Semiconductor Surfaces
**Moderator:** S. Bent, Stanford University

**2:00pm SS2-MoA1 Comparative Molecular Surface Functionalization of Silicon Surface Structures**, *D.E. Barlow, S.C. Erwin, A.R. Laracuente, L.J. Whitman, **J.N. Russell***, Naval Research Laboratory
Methods and chemistries to covalently attach organic molecules to single crystal semiconductor surfaces are the subject of considerable interest. While past functionalization studies on silicon have focused primarily on the (001) surface, the Si(114), oriented 19.5° between (001) and (111), has an equilibrium surface reconstruction comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction. These structures make Si(114) an ideal surface for elucidating relationships between surface structure and organic reaction mechanisms on silicon. We have investigated cyclopentene and ethylene chemisorption on Si(114) using transmission Fourier transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM) and density-functional-theory (DFT) calculations. The FTIR spectra are consistent with di-sigma bonding. A detailed analysis of the strong angular and polarization dependence of the ethylene C-H stretching mode intensities indicates it chemisorbs with the C-C bond axis parallel to the structural rows oriented along the [(1)10] surface direction. Using atomic-resolution STM, we identified three common adsorption structures located at the dimer, rebonded atom, and tetramer sites. In correlation with the FTIR and DFT results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of surface site reactivity is found to be rebonded atoms > dimers > tetramers. We found each ethylene/Si(114) adsorption structure has a characteristic C-H vibrational signature, which we used to identify the ethylene molecules that are chemisorbed on the step edges of the 4° off-axis (single domain) Si(001) surface.

**2:20pm SS2-MoA2 Adsorption of Ethanethiol, Ethanol, and Mercaptoethanol on Ge(100)-2x1**, ***J.S. Kachian***, *S.F. Bent,* Stanford University
The adsorption of ethanethiol, ethanol and mercaptoethanol on Ge(100)-2x1 at 310 K was investigated to gain a fundamental understanding of bonding in these systems for use in practical applications surrounding semiconductor passivation. Vibrational spectra of the products of these three reactions obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy in ultrahigh vacuum suggest that the products are formed via dissociation of the X-H bond, where X represents the electronegative atom(s)-O and/or S--in the adsorbate. It is believed that these reactions are preceded by a dative-bonded state in which the electronegative atom of the adsorbate donates a lone pair of electrons to the down atom of a germanium dimer. Density functional theory was used to investigate this pathway, and potential energy surfaces and frequency spectra obtained by calculation support the postulated mechanism. The results will be discussed in the context of relative reactivity of S versus O groups. Further, these results can be applied towards the analysis of larger molecules, which contain reactive centers in addition to that of a thiol or alcohol group. Of particular interest is the thiol-containing amino acid cysteine. This molecule, which introduces competition between thiol, amino and carboxyl moieties, is largely responsible for the formation of disulfide bonds in proteins, thus leading to stable three-dimensional protein structure. Understanding the reactivity of the thiol moiety in the context of a biologically relevant molecule brings the concept of nanoscale biosensors one step closer to reality.

**2:40pm SS2-MoA3 The Cycloaddition of Organic Molecules to the Si(100)c(4x2) Surface: Microscopic Mechanism and Tunneling Properties of Single Molecules**, *J. Yoshinobu,* University of Tokyo, Japan     **INVITED**
Chemical modification of Si surfaces has attracted much attention from the view point of coating, sensors, molecule-based microelectronics and so on. The cycloaddition of organic molecules to the Si(100) surface is the most important family of chemical reactions for the modification of the Si surface as well as Lewis acid-base reaction, because the stable Si-C covalent bonds are formed between molecules and the surface. In the cycloaddition, the asymmetric dimer on the reconstructed Si(100) surface plays an important, in which a partial charge transfer occurs from a down dimer atom (Sd) to an up dimer atom (Su). The chemical nature of Sd and Su is electrophilic and nucleophilic, respectively; the asymmetric dimer may act as a zwitter ion. In this talk, first, we show some examples of regioselective

cycloaddition reaction between asymmetric alkene molecules and the asymmetric dimer on Si(100)c(4x2) using low-temperature STM. The regioselective cycloaddition product may be controlled by a precursor state. Next, scanning tunneling spectroscopy (STS) results of a single adsorbed molecule will be presented. In some cases, interesting features are observed in I vs.V characteristics, which may be due to adsorbate derived local electronic states.

**3:20pm SS2-MoA5 Passivation of Germanium and Silicon Surfaces with Oxide, Hydrogen, Chlorine, and Methyl**, ***S. Rivillon Amy***, *Y.J. Chabal,* Rutgers University*; F. Amy, A. Kahn,* Princeton University
Chemical passivation of semiconductor surfaces represents an important part of front end processing for CMOS and other microelectronics applications. The industry has been based primarily on silicon (Si) technology due to the remarkable properties of its oxide, but there is a need to explore higher mobility substrates such as germanium (Ge). Although Si and Ge are both group IV semiconductors, it is well-known that their chemical properties differ dramatically. In particular, Ge has a variety of rather unstable oxides and cannot be chemically passivated as easily as Si. The focus of this talk is on comparing the passivation of germanium surfaces with oxide, hydrogen, chlorine, and methanol to that of the corresponding species on silicon, which have been well characterized. The main characterization techniques to monitor the chemical state of the surface are infrared absorption spectroscopy (IRAS) and X-rays photoelectron spectroscopy (XPS). Besides the formation of much more complex and less stable oxides on Ge, we confirm that H-termination of Ge in HF solutions is much more delicate and invariably leads to atomically rough surfaces with predominance of dihydrides on Ge(100) and trihydrides on Ge(111). To compensate for variation in "native" oxide thickness, a procedure involving $H_2O$ rinsing, oxidation by $H_2O_2$ immersion and dilute (10 vol%) HF (or HCl) etching has been developed, which reliably leads to H- (or Cl-) termination. XPS data confirm the presence of chlorine (Ge-Cl and $Ge-Cl_2$) on Ge(100) surface. The stability of both H- and Cl-terminated surfaces is similar: poor in air but stable in clean $N_2$ environment. The results of methanol adsorption on Ge and Si surfaces illustrate the propensity for Ge to bind with C, which constitutes a clear drawback for microelectronics applications.

**3:40pm SS2-MoA6 Photochemical Functionalization and Chemical Patterning of Gallium Nitride Thin Films with Biomolecular Layers**, *H. Kim, P. Colavita, K. Metz, B.M. Nichols, B. Sun, J.J. Uhlrich, X. Wang, T.F. Kuech, R.J. Hamers,* University of Wisconsin at Madison
Gallium nitride is a particularly intriguing semiconductor for sensing applications because it can be grown as a thin crystalline film and because the high ionic character of GaN causes the intrinsic surface states to be near the respective band edges, where they have less impact on the interfacial electronic properties. We have investigated the functionalization of gallium nitride (0001) surfaces with well-defined molecular and biomolecular layers. After cleaning in a hydrogen plasma, GaN surfaces were reacted photochemically with organic alkenes bearing protected amine groups using ultraviolet light. Using a simple contact mask to control the UV light, we demonstrate the ability to directly pattern chemical groups onto the surface with a spatial resolution of <12 microns. After linking to the surface, the molecules groups were deprotected and used to link DNA oligonucleotides to the GaN surface. Measurements using fluorescently labeled complementary and non-complementary sequences showed that the DNA-modified GaN surfaces exhibit excellent selectivity, and repeated cycles of hybridization and denaturation show good stability. These results demonstrate that GaN can be used as an alternative substrate for molecular and biological sensing applications.

**4:00pm SS2-MoA7 Achieving a Low Surface Recombination Rate Despite a High Surface Defect Density: the Role of Charge Carrier Concentration**, ***D.J. Michalak***, *N.S. Lewis,* California Institute of Technology
Low interfacial electron-hole recombination rates are essential for low-noise electronic devices and high-efficiency solar energy converters. This interfacial recombination rate is dependent on both the electrical trap state density, $N_T$, and the concentrations of electrons, $n_s$, and holes, $p_s$.[1] Reports of low recombination rates have often been attributed to a low $N_T$,[2] without a measurement of $n_s$ and $p_s$, partly because the importance of $n_s$ and $p_s$ has not been fully recognized and partly because an accurate evaluation of $n_s$ and $p_s$ can be difficult. In this work, surface recombination rates of stable silicon/liquid junctions, observed using a contactless rf photoconductivity technique,

were compared with $n_s$ and $p_s$ values obtained from Mott Schottky analysis. Our results demonstrate that recombination rates can only be correlated with $N_T$ when $n_s = p_s$. Otherwise, the recombination rate was always low due to a large $n_s$ or $p_s$ even in the presence of a large $N_T$. The full impact of this work was further realized through a study of the recombination rates of H-Si immersed in solutions of 48% HF, 40% $NH_4F$, or buffered HF (BHF) because such measurements are often performed for in situ monitoring of the surface quality during wafer processing steps. Our results demonstrate that only HF contacts can be used for in situ monitoring because $n_s = p_s$. For $NH_4F$ or BHF contacts, low recombination rates were observed only because $n_s$ is much larger than $p_s$, and no information about $N_T$ can be inferred from these measurements. [FootnoteText] [footnote 1] Hall, R.N., Physical Review 1952, 87, (2), 387, and Shockley, W., and Read, W.T., Physical Review 1952, 87, (5), 835-842.[footnote 2] Msaad, H., et al., J. Electron. Mater. 1994, 23, (5), 487-491, and Yablonovitch, E. et al., Phys. Rev. Lett. 1986, 57, (2), 249-252.

4:20pm **SS2-MoA8 Reaction of Amino Acids on the Ge(100) Surface**, *S.J. Jung,* Korea Advanced Institute of Science and Technology (KAIST)*; J.S. Kachian,* Stanford University*; S. Kim,* Korea Advanced Institute of Science and Technology (KAIST)*; S.F. Bent,* Stanford University

The adsorption of amino acids on the Ge(100) surface was investigated with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, scanning tunneling microscopy (STM) and density functional theory. All amino acids consist of a carboxylic acid (-COOH) and an amino (-$NH_2$) functional group attached to the same tetrahedral $\alpha$-carbon atom. Amino acids are distinguished by the different R-groups attached to the $\alpha$-carbon. The simplest amino acid is glycine, with an H as the R-group. Our MIR-FTIR results indicate that for glycine, the principal surface product is formed by OH dissociation of the carboxylic acid group. This result is consistent with calculations, which indicate that the OH dissociation product is the most thermodynamically stable. More than one surface product is evident in the spectra, however, with the results suggesting products containing nitrogen dative bonds. Based on the understanding of glycine, the effect of the side chain can be probed in more complex amino acids. Histidine ($C_6H_9N_3O_2$), a basic amino acid, has an imidazole group as the R-group. STM results reveal the ordering of histidine molecules on the Ge(100) surface. At saturation coverage, the STM images show globally ordered arrays consisting of dumbbell shape features that are independent of the direction of the underlying dimer rows of the Ge (100) surface. We will present the adsorption structures and discuss the role of adsorbate-adsorbate intermolecular interactions based on the experimental results and ab initio calculations of glycine. The studies of glycine and histidine allow us to understand the competitive tendencies of the amine and carboxylic acid functional groups in amino acids and also identify the reactivity of the moieties present in the side chain. These results provide a basis for future studies of amino acid polymers, i.e. proteins, which can be used in biocompatible materials of the future.

## Surface Science
## Room 2002 - Session SS1-TuM

### Reactivity of Metal Clusters
**Moderator:** A.J. Gellman, Carnegie Mellon University

**8:00am SS1-TuM1 Thermal Stability of Metallic Nano-Clusters and Film Patterning on Solid Surfaces Studied Via Weakly Bound Buffer Layer**, *M. Asscher,* Hebrew University, Israel

Growth of metallic nano-clusters and control over their size are critically important for catalysis. Development of film patterning at the nanometer scale has significant impact on future lithography. In this work we combine a method to deposit metallic nano-clusters using weakly bound buffer layer as an intermediate substance to control the clusters size with laser patterning that modulates their surface density. Using optical probes, the size selected diffusion of gold nano-clusters on metallic and oxygen modified surfaces has been studied. Information on clusters mobility is critical for understanding and control the thermal stability of clusters toward the development of sintering resistant catalysts. The same technique was further developed at thicker film thickness to pattern the layer at the sub-micron to nanometer scale employing a single laser pulse. This technique is discussed as a novel approach for lithography.

**8:20am SS1-TuM2 CO and NO Reactions over Rh Nanoparticles Supported on Ceria Thin Films@footnote 1@**, *S.D. Senanayake, D.R. Mullins,* Oak Ridge National Laboratory

The reduction of noxious automotive emissions such as CO and NO@sub X@ with the use of solid catalysts is of great importance at present due to ever tightening regulatory standards for gas emissions. Novel catalysts consisting of metal particles supported on various oxide surfaces are often employed. The oxidation reaction of CO to CO@sub 2@ and the sequential reduction of NO to N@sub 2@ are frequently found to be strongly dependent on the composition and oxidation state of the oxide support. In this work we investigated reactions over one such catalytic system, Rh/CeO@sub X@, with the use of temperature programmed desorption (TPD), soft x-ray photoelectron spectroscopy (SXPS) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy. The CeO@sub 2@ and CeO@sub X@ surfaces are grown in situ by evaporation of Ce in a low-pressure O@sub 2@ ambient (1x10@super -7@ Torr) on a Ru(0001) single crystal. Rh nanoparticles are subsequently deposited onto this surface. Isotopic labeling of the substrate (Ce@super 18@O@sub X@) and reactants (@super 13@CO and @super 15@NO) were used to elucidate reaction mechanisms. Surface intermediates are identified using SXPS and NEXAFS performed at Beamline U12a at the NSLS. In addition we also present preliminary results of this same reaction under dynamic reaction conditions. The pressure gap is a very difficult obstacle to overcome in the study of real time reaction dynamics under UHV conditions. We have addressed this problem by using an effusive molecular beam of CO and NO produced by a directed-doser attached to the UHV system. We have compared the reaction on a Rh(111) single crystal surface with that on Rh nanoparticles supported on ceria. @FootnoteText@ @footnote 1@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.

**8:40am SS1-TuM3 Size Dependent Composition and Catalytic Reactivity of Platinum Clusters from First Principles**, *W.F. Schneider,* University of Notre Dame **INVITED**

Three central questions have emerged in nanoscale heterogeneous catalysis: First, how does the structure and catalytic function of transition metal catalysts evolve as particles decrease in size from the micro to the nanoscale? Second, how do these particles interact and communicate with supports, and what are the effects on structure and reactivity? Third, how does the particle/support system respond to realistic and dynamic reaction environments? In this work we use first-principles density functional theory methods to consider these three questions in the context of oxidation catalysis on 1-10 atom Pt clusters. Using DFT-parameterized thermodynamic models, we explore the structure and compostion of the clusters as a function of oxidation conditions, illustrating the pronounced tendency to become partially to completely oxidized under most practically relevant conditions.@footnote 1@ This tendency is shown to persist but to be modified in clusters supported on an undefected MgO surface. To probe the consequences of environment and support on reactivity, we constrast

the reactivity of the clusters toward strong (CO) and weak (NO) reductants. The results illustrate that both particle size and reactive environment can have a signficant influence on the reactivity of metal clusters and start to clarify the origins of these effects. @FootnoteText@ @footnote 1@ Y. Xu, W. A. Shelton, and W. F. Schneider, "Effect of Particle Size on the Oxidizability of Platinum Clusters," J. Phys. Chem. A, 2006, in press.

**9:20am SS1-TuM5 Formic Acid Decomposition on Pd Nanoparticles Deposited on TiO@sub 2@(110)**, *J. Zhou, S. Dag, V. Meunier, S.V. Kalinin, D.R. Mullins, S.H. Overbury, A.P. Baddorf,* Oak Ridge National Laboratory

Adsorption and dissociation of formic acid molecules on clean TiO@sub 2@(110) and on TiO@sub 2@(110) with deposited Pd nanoparticles were investigated using scanning tunneling microscopy (STM), temperature programmed desorption (TPD) and first-principles calculations. Our TPD data indicate that formic acid can decompose on bare titania and produce CO, CO@sub 2@, H@sub 2@ and H@sub 2@O upon heating after adsorption at 110 K. H@sub 2@ was detected in multiple peaks between 200 K and 600 K, while CO and CO@sub 2@ desorbed with a single peak around 550 K and H@sub 2@O evolved at 270 K. After deposition of Pd to titania, formic acid dissociation was greatly enhanced. Furthermore, multiple CO, CO@sub 2@ and H@sub 2@ desorption peaks were observed. At 300 K, individual species were seen bonded to the atomic Ti rows in the STM image, due to the formate formation after adsorption. Bonding of formate on reduced 1x2 strands was also observed in our study. Formate was further identified near and on Pd particles by STM at 300 K. Upon heating to 375 K, formate reacted to form a new species observed bridging the Ti rows. An atomic scale understanding of the experimental STM images is provided from detailed first-principles calculations. Research was sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC for the U. S. DOE under Contract DE-AC05-00OR22725.

**9:40am SS1-TuM6 Pd Cluster Growth on the SnO2 (101) Surface**, *Kh. Katsiev, U. Diebold, M. Batzill,* Tulane University

Tin oxide is widely used as a solid-state gas sensor for detection of combustible and toxic gases. Its sensitivity and selectivity can be enhanced by catalytically active dopants such as Pd. We have studied the growth of Pd on the SnO2 (101) surface in the sub-monolayer regime using STM, XPS, ARUPS and LEED. The SnO2(101)-(1x1) surface was prepared in stoichiometric (Sn(IV)) and in full- reduced (Sn(II)) form. Palladium was vapor-deposited on both surfaces at room temperature. On the stoichiometric surface round 3-D clusters with an average size of ~1 nm nucleate at surface defects. On the reduced surface, 1-D nanostructures form on the terraces; these are imaged in STM as straight, parallel structures, all with the same characteristic width of one substrate unit cell and height of one ML. The length of the Pd clusters is limited by the size of the substrate's terraces. XPS shows metallic Pd with a 0.45 eV shift in the Pd 3d core level peak position to lower binding energy during the initial stages of the growth. ARUPS measurements show that the position of the Pd-4d valence band "follows" the position of the Sn-5s derived surface state for the reduced SnO2(101) surface. This indicates a strong electronic interaction between the Sn-5s state and the Pd d-band. Clusters nucleated at sputter-created defects are wider and shorter. From LEED it appears that the 1D clusters are commensurate with the substrate in one direction. Formic acid adsorbs on the 1D nanoclusters, but not the SnO2 surface at RT. The clusters are thermally not stable, they coarsen upon annealing to a temperature of 200°. DFT calculations of various test structures suggest that the formation of the 1-dim clusters is dominated by kinetic effects. Pronounced one-dimensional diffusion, combined with strong interaction between Pd and surface Sn appear to be responsible for the formation of the one-dimensional islands.

**10:40am SS1-TuM9 New Atomic-Scale Insights Into Promoter and Support Effects on MoS@sub 2@ Nanoclusters from STM Studies of Hydrotreating Model Catalysts**, *J. Kibsgaard, J.V. Lauritsen,* University of Aarhus, Denmark*; H. Topsøe, B.S. Clausen,* Haldor Topsøe A/S, Denmark*; F. Besenbacher,* University of Aarhus, Denmark

To meet the stringent requirements for upgrade and clean-up of transport fuels by hydrotreating there is currently an urgent need to understand and improve the MoS@sub 2@-based catalyst applied for this service. The active phase of this catalyst is composed of 2-3nm wide MoS@sub 2@-like nanoclusters, typically promoted by Co or Ni, forming the so-called CoMoS and NiMoS nanostructures. Despite intense research efforts, the morphology of CoMoS and NiMoS and the detailed location and coordination of the promoter atoms have not been resolved. Consequently, the role of the Co and Ni is poorly understood, and existing

models are not able to account for the difference in the specific selectivity of Co or Ni promoted catalysts with respect to hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD). In this study, we present atom-resolved scanning tunneling microscopy (STM) of CoMoS and NiMoS nanoclusters supported on Au(111). In the STM images we observe a promoter dependent morphology, which is explained by the different affinities for Co and Ni to replace Mo at the edge sites of MoS@sub 2@ nanoclusters. This finding shows that the location and coordination of the promoter atoms are different in CoMoS and NiMoS, which may explain the different selectivity observed in the industrial catalysts. In order to include the effect of a different support, we also synthesized MoS@sub 2@ nanoclusters on highly oriented pyrolytic graphite (HOPG). HOPG as a substrate is indeed very interesting since carbon-supported hydrotreating catalysts have previously been found to exhibit very high HDS reactivity. STM images reveal that the morphology of the MoS@sub 2@ nanoclusters is very dependent on the exact preparation temperature. Furthermore, images of the top facet of the clusters provide new atomic-scale information on the MoS@sub 2@-HOPG topotaxy, and we find good correspondence between the edge structure and previous studies of MoS@sub 2@ on an Au substrate.

**11:00am SS1-TuM10 Deposition and Reactivity of Mo@sub x@S@sub y@ (x/y=4/6, 6/8, 7/10) Clusters on Au(111)**, *J.M. Lightstone, M.J. Patterson, J. Lofaro,* Stony Brook University*; P. Liu, M.G. White,* Brookhaven National Laboratory

We have recently constructed a cluster deposition apparatus which employs a magnetron sputtering source for generating gas-phase cation clusters of pure metals and metallic compounds. Our current focus has been the production of early transition metal sulfide clusters for reactivity studies in both the gas-phase and deposited on well defined surfaces. The transition metal sulfides are particularly interesting due to their catalytic properties@footnote 1@ and their ability to form fullerene-like nanostructures that reflect the S-M-S layered structure of the bulk materia.l@footnote 2@ The work reported here examines preliminary electron spectroscopy and temperature programmed desorption results from size-selected Mo@sub x@S@sub y@ (x/y=4/6, 6/8 and 7/10) clusters deposited on a Au(111) single crystal. A wide array of molybdenum sulfide clusters, Mo@sub x@S@sub y@@super +@ (x/y= 2/6, 3/7, 4/6, 5/7, 6/8, 7/10, 8/12), were generated using a magnetron sputtering source, including the "magic" number species Mo@sub 4@S@sub 6@@super +@. Several Mo@sub x@S@sub y@@super +@ clusters were mass selected using a quadrupole mass spectrometer and deposited on a Au(111) single crystal under ultra-high vacuum conditions. The presence of deposited clusters was confirmed using Auger Spectroscopy (AES) while Ultraviolet and X-Ray Photoelectron Spectroscopy (UPS, XPS) were used to probe the electronic structure of the cluster covered surface. Temperature Programmed Desorption (TPD) of carbon-13 labeled CO shows cluster-dependent desorption peaks which were used to estimate CO binding energies. The TDP spectra are also found to depend on annealing temperature, which suggest surface modifications or cluster decomposition at higher temperatures. @FootnoteText@ @footnote 1@T. R. Thurston and J. P. Wilcoxon, J. Phys. Chem. B, 103 (1997) 11.@footnote 2@R. Tenne and C. N. R. Rao, Phil. Trans. R. Soc. Lond. A, 362 (2004) 2099.

**11:20am SS1-TuM11 The Structure of Catalytically Active Gold**, *M.S. Chen, D.W. Goodman,* Texas A&M University

Well-ordered Au mono- and bi-layer films were synthesized on a TiOx/Mo(112). The wetting of Au on the (8x2)-TiOx is clearly evidenced by recent STM studies, and the ordered (1x1) mono- and (1x3) bi-layer structures are atomic resolved. The electronic and chemical properties of these ordered Au films were characterized by IRAS using CO as a probe molecule and UPS. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the Au bi-layer structure is significantly more active (by more than an order of magnitude) than the monolayer, and is about 45 times higher than that reported for the most active higher-surface-area Au/TiO2 catalyst. The common structural features of ordered Au bi-layers and Au bi-layer nanoparticles on TiO2(110) are described, the nature of the active site and structure of supported Au catalysts are discussed, and the exceptionally high catalytic activity of the Au bi-layer structure are related to its unique electronic properties.

**11:40am SS1-TuM12 Novel Gold Catalysts: UHV and Ambient Studies on Nanoporous Gold Surfaces**, *M. Baeumer, T. Nowitzki, B. Juergens, C. Schulz, V. Zielasek,* University Bremen, Germany*; J. Biener, M. Biener, A.V. Hamza,* Lawrence Livermore National Laboratory

While a lot of questions regarding the underlying mechanisms of gold catalysis are still under debate, it is evident that low-coordinated Au atoms play a decisive role for reactions such as the low-temperature oxidation of CO, for instance. In order to elucidate how low-coordinated Au atoms can be stabilized and in which way they interact with CO, we performed UHV model studies pursuing two different approaches. On the one hand, a Au(111) single crystal surface was sputtered by argon and oxygen ions, resulting in rough pit-and-mound structures. Annealing experiments clearly revealed that the oxygen sputtered surface exhibits a higher thermal stability, indicative of the stabilization of under-coordinated Au atoms by adsorbed oxygen. In both cases, two CO TPD desorption peaks are observed between 100 K and 200 K. For the oxygen sputtered surface also CO2 formation is detected concurrently with desorption of CO. On the other hand, Au was deposited on graphite as a weakly interacting support. Interestingly, the same TPD spectrum with 2 peaks is found in this case. Deposition under various conditions (variation of the support temperature, defect-assisted growth) reveals that both states are defect-related. In line with theoretical results, one state may be attributed to step edges, the other to even less coordinated sites. As a similar desorption behaviour was observed for other particle systems and rough single crystal surfaces, this seems to be a general feature. In addition to the UHV studies, we performed catalytic studies with a gold foam prepared by dealloying of a Ag/Au alloy. It exhibits a very similar morphology as compared to the sputtered Au(111) surface. We could demonstrate that this material has an unexpectedly high catalytic activity for CO oxidation at temperatures down to -20 °C. @FootnoteText@ Part of this work was performed under the auspices of the U.S. Dep. of Energy by Univ. of California, Lawrence Livermore National Laboratory under contract No.W-7405-Eng-48.

## Surface Science
## Room 2004 - Session SS2-TuM

### Water-Surface Interactions

**Moderators:** A.A. Baski, Virginia Commonwealth University, M. Salmeron, Lawrence Berkeley National Laboratory

**8:20am SS2-TuM2 Reactions of Ozone with the Constituents of Sea Salt Particles**, *M.A. Brown, M.J. Krisch, J.T. Newberg,* University of California, Irvine and AirUCI*; B.S. Mun,* Lawrence Berkeley National Laboratory*; J.C. Hemminger,* University of California, Irvine and AirUCI

The uptake and then destruction of ozone on the surface of alkali halides is thought to play an important role in the chemistry of the troposphere and is believed to generate gas phase molecular halogens in the atmosphere. We present the results from both lab based UHV XPS and ambient pressure XPS at LBNL Advance Light Source beamline 9.3.2 on the reactive uptake of ozone at both the vapor solid and vapor liquid interfaces of alkali halide salts. Ozone proves to be a strong oxidizer and iodide salts are surface oxidized to iodates. Uptake measurements for both the bromide and chloride salts will also be presented. Through the use of surface imaging techniques at the Molecular Foundry of LBNL insights into the site specificity of the reaction are explored.

**8:40am SS2-TuM3 Nanocarpet Effect: Formation and Characterization of Watermarks on Aligned Silicon Nanorod Arrays**, *Y.P. Zhao, J.G. Fan,* University of Georgia

When a water drop spreads on an aligned silicon nanorod surface prepared by glancing angle deposition, a watermark developed on the surface after water evaporated due to the bundling of nanorods. The watermark radius R follows a simple power law relationship with the water volume @OMEGA@ as R ~ @OMEGA@@super n@. The scaling exponent n, in the vicinity of 1/3, increases when the nanorods height decreases. This behavior is attributed to the competition of evaporation and spreading of a water droplet during the spreading process. The size of the bundled nanorod cluster depends not only on the nanorod height, but also on the location in the watermark. The cluster size almost remains as a constant near the center, and then it decreases with the distance from the center. This phenomenon can be qualitatively interpreted through the change of the total free energy during the precursor invading the nanorod array, by considering the contribution from the mechanical energy change due to the bending and clustering of nanorods.

# Tuesday Morning, November 14, 2006

**9:00am SS2-TuM4 Lateral Water Ordering at Reconstructed MgO(111) Surfaces**, *P.F. Lyman, S.S. Parihar, H.T. Johnson-Steigelman, V.L. Shneerson, R. Fung, D.K. Saldin,* University of Wisconsin-Milwaukee*; F.U. Renner, T.-L. Lee, J. Zegenhagen,* ESRF, Grenoble, France

The polar oxide surface MgO(111) is known to undergo several air-stable reconstructions, including p(2x2) and (@sr@3x@sr@3)R30° phases. The observed structure depends on O partial pressure and temperature. We report on a study of stability and structure of these reconstructions at an aqueous interface. The interface between the bulk water layer (5 μm) and the reconstructed MgO(111) was probed using surface x-ray diffraction. For other substrates, previous measurements of the specular surface truncation rod had revealed that a surface can induce layered ordering in the interfacial water, but measurements of off-specular rods indicated that only weak lateral ordering was present.@footnote 1@ Our study addressed the additional effect of a corrugated, reconstructed interface. Moreover, reflections with smaller in-plane momentum transfers are available when using a reconstructed surface, allowing more sensitive studies of any lateral ordering. For the (@sr@3x@sr@3)R30° phase, the reconstruction was stable in contact with water for many hours. Changes (between wet and dry interfaces) in the non-specular rods closest to the origin (in reciprocal space) reveal changes in the ordered lateral electron density, presumably due to lateral ordering in the water layer. The p(2x2) surface roughened and de-reconstructed almost immediately upon immersion in water. @FootnoteText@ @footnote 1@M.F. Reedijk et al., Phys. Rev. Lett. 90, 066103 (2003) .

**9:20am SS2-TuM5 2006 Medard W. Welch Award Lecture - Surface Composition and Surface Chemistry of Alkali Halide Solids and Aqueous Solutions**, *J.C. Hemminger[1],* UC, Irvine*; M.J. Krisch, M.A. Brown,* UC, Irvine and AirUCI*; S. Ghosal,* LLNL*; H. Bluhm, B.S. Mun,* LBNL*; A. Verdaguer,* Institut Catala de Nanotecnologia, Spain*; F. Ogletree, M. Salmeron,* LBNL **INVITED**

Chemistry at the surfaces of aerosol particles in the troposphere has become a topic of considerable interest recently. Reactions between gas phase molecules in the atmosphere and aerosol particles and droplets may modify the properties of the aerosol (such as hydrophobicity or chemical composition). In addition, components of the aerosol may be converted into volatile compounds that can then be active in gas phase reactions in the troposphere. Clearly, the composition of the surfaces of such particles will control their surface reactivity. We have studied models for sea salt aerosols, which are abundant in the marine region world-wide. We have shown that adsorbed water is critical to the surface chemistry of salt surfaces. In addition, recent molecular dynamics simulations of alkali halide solutions have suggested that the surfaces of alkali halide solutions are enriched in halide species. Our experiments quantitatively confirm that the surfaces of aqueous KI, KBr and KCl solutions have enhanced halide ion concentrations. Additionally, experiments on Br doped NaCl samples show conclusively that Br strongly segregates to the liquid-vapor interface of such mixed solutions. A combination of data from scanning polarization force microscopy experiments and x-ray photoelectron spectroscopy experiments will be shown to illustrate these phenomena. The importance of these results to atmospheric chemistry will be illustrated through a discussion of bromine segregation in sea salt aerosols and the importance of the subsequent bromine chemistry in the arctic marine troposphere.

**10:40am SS2-TuM9 Growth and Structure of Water on Amorphous SiO2 Investigated by Kelvin Probe Microscopy and In Situ X-ray Photoelectron Spectroscopy**, *M. Salmeron,* Lawrence Berkeley National Laboratory*; A. Verdaguer,* Institut Catala de Nanotecnologia, Spain*; G. Ketteler, Ch. Weiss, H. Bluhm, D.E. Starr,* Lawrence Berkeley National Laboratory

The growth and structure of water layers on SiO2 on Si wafers at pressures between 1 and 4 torr and temperatures between -10 and 21 C has been studied using Kelvin Probe Microscopy and in situ X-ray photoelectron spectroscopy. As the relative humidity (RH) increases from 0 to 75% water adsorbs forming of a uniform film up to a thickness of 4 to 5 layers. The surface potential increases in that range by about 120 mV and remains constant afterwards. Above 75% RH the film grows rapidly reaching 6 to 7 monolayers at 90%. The near-edge X-ray adsorption spectra is similar to that of liquid water (imperfect H-bonding coordination) after the first four layers. At all stages the presence of unsaturated dangling H-bonds in the outermost layer in contact with the vapor is visible.

**11:00am SS2-TuM10 A Combined Droplet Train / Photoemission Spectroscopy Experiment for the Investigation of Heterogeneous Reactions on Liquid Surfaces**, *D.E. Starr,* K.R. Wilson, H. Bluhm, Lawrence Berkeley National Laboratory

The properties of liquid/vapor interfaces strongly influence the abundance and reactivity of trace gas molecules that are important for many heterogeneous processes in atmospheric and environmental chemistry. A direct measurement of the liquid/vapor interface under atmospherically and environmentally relevant conditions is difficult due to the lack of quantitative experimental techniques that are surface-sensitive, chemically specific and can operate at elevated pressures in the Torr range. Here we describe a novel experimental setup that is operating at beamline 11.0.2 at the Advanced Light Source in Berkeley. The instrument combines synchrotron-based ambient pressure photoemission spectroscopy (APPES, operating at pressures of more than 5 Torr) and a liquid droplet train produced by a vibrating orifice aerosol generator (VOAG). In a VOAG, droplets of uniform size (5-100 Î@micron@) are generated by forcing the liquid under investigation through a vibrating orifice. The short time (milliseconds) between the generation of the droplets at the vibrating orifice and their measurement in the spectrometer minimizes the level of contamination of the surface. Beam damage is kept at a minimum since each droplet is irradiated only for a few microseconds by the incident X-rays. In addition, the interaction time of the droplet surface with gas molecules can be varied over a range from about 1 to 20 ms, allowing for measurements of the reaction kinetics at liquid surfaces as a function of exposure time to a gaseous environment. Studies of the role of liquid surface species in the transport of gas molecules across the liquid/vapor interface, as well as studies of surface-mediated chemical reactions at the liquid/vapor interface are also possible.

**11:20am SS2-TuM11 Ion Depth Profiles at the Liquid - Vapor Interface of Electrolytes in Mixtures of Water and Alcohol**, *M.J. Krisch,* M.A. Brown, R. D'Auria, K.M. Callahan, D.J. Tobias, J.C. Hemminger, University of California at Irvine*; M. Ammann,* Paul Scherrer Institute*; H. Bluhm,* Lawrence Berkeley National Laboratory

We find that organic compounds modify the interfacial profile of electrolytes in aqueous solutions. Our experiments probe atomic composition at the liquid surface with ambient pressure x-ray photoelectron spectroscopy at the Advanced Light Source. Photoelectron kinetic energies are varied to produce a depth profile of the liquid - vapor interface. Surface enhancement of iodide anions, an effect observed in aqueous potassium iodide solution, disappears in the presence of a surface active alcohol such as 1-butanol. Results are compared to molecular dynamics simulations of the same system. Insight into ion behavior at mixed liquid surfaces is crucial for understanding the chemistry of atmospheric aerosols, which frequently contain ternary mixtures of water, electrolytes, and organics.

**11:40am SS2-TuM12 Interfacial Water Structure and Dynamics Probed with Chemical Force Microscopy**, *P.D. Ashby,* M. Salmeron, Lawrence Berkeley National Laboratory

Understanding the structure and energetics of water at interfaces is important for many diverse fields of study including self-assembly of nanostructures, protein folding, tribology, and catalysis. Two novel methods for investigating interfacial water structure with the Atomic Force Microscope will be presented. First, Brownian Force Profile Reconstruction harnesses cantilever thermal motion to accurately and precisely reconstruct equilibrium force profiles. Experiments between solvated hydroxyl terminated self-assembled monolayers revealed highly oriented water structure which decayed into the bulk within three molecular layers. Second, Tapping Mode Force Profile Reconstruction computes the forces experienced by the advancing and receding tip surface during high frequency oscillation. Investigation of solvated hydrophilic surfaces revealed slow reordering dynamics in electrostatic doubles layers and fast reordering for less long range interactions.

**12:00pm SS2-TuM13 The Adsorption and Uptake of Acetone on Ice Studied with Ambient Pressure Photoemission Spectroscopy**, *D.E. Starr,* Lawrence Berkeley National Laboratory*; M. Ammann,* Paul Scherrer Institute*; H. Bluhm,* Lawrence Berkeley National Laboratory

The interaction between small molecules and ice particles has broad implications in atmospheric chemistry. While many experimental techniques, such as flow tube and Knudsen cell measurements and laser based spectroscopic techniques, have provided a great deal of insight into the kinetics and mechanisms associated with these reactions, most of these techniques lack the ability to chemically identify the species directly

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

adsorbed on the ice surface. On the other hand, surface science techniques are particularly well-suited for exactly this purpose but generally require Ultra-High Vacuum to be utilized, precluding their use under atmospherically relevant conditions where the vapor pressure of ice is in the mTorr to Torr range. With the development of synchrotron-based Ambient Pressure Photoemission Spectroscopy (APPES) the chemical identification of adsorbed molecules on the ice surface at atmospherically relevant conditions becomes possible. As an initial step in these studies we have investigated the adsorption and uptake of acetone on the ice surface. The sequestering of acetone by ice particles in the atmosphere and polar snowpack may play an important role in atmospheric chemistry due to acetoneâ?Ts role as a radical source in the upper troposphere and radical chemistry in polar snowpack. In addition, the acetone/ice system is believed to be a fairly simple, reversible adsorption system. Uptake measurements using the integrated C1s peak area as a function of acetone partial pressure indicate an adsorption energy of approximately 45 kJ/mol. In addition, high resolution C1s spectra as well as O K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) both show little to no modification of the acetone molecule or the ice surface upon adsorption. The combined results indicate a weak interaction between the acetone molecule and ice surface under ambient conditions.

# Tuesday Afternoon, November 14, 2006

## Surface Science
## Room 2002 - Session SS1-TuA

### Surface Structure and Morphology

**Moderator:** S. Chiang, University of California, Davis

**2:00pm SS1-TuA1 Interfacial Strains in Nanocrystals Revealed by Coherent X-ray Diffraction**, *I.K. Robinson,* University College and Diamond Light Source, UK **INVITED**
Nanocrystals are fundamentally different from the bulk because strain can build up more easily inside the lattice.@footnote 1,4@ Interface from a nanometre-sized crystal to an adjacent material can lead to pattern formation, which can be very dramatic. X-ray diffraction is a generally useful way to measure structure at the atomic level. Recent development of methods exploiting the very high coherence of the latest sources have allowed direct imaging of crystal shapes at lower-than-atomic resolution.@footnote 2@ We have developed a new method to retrieve 3D complex density functions that reveal these strains.@footnote 3@ We will report new results in which interfacial strains between lead nanocrystals and $SiO_2$ substrates have been observed. @FootnoteText@ @footnote 1@"Partial Coherence Effects on the Imaging of Small Crystals using Coherent X-ray Diffraction", I. A. Vartanyants and I. K. Robinson, Journal of Physics Condensed Matter 13 10593-611 (2001)@footnote 2@"Three-dimensional Imaging of Microstructure in Gold Nanocrystals", G. J. Williams, M. A. Pfeifer, I. A. Vartanyants and I. K. Robinson, Physical Review Letters 90 175501-1 (2003)@footnote 3@"Three Dimensional X-ray Diffraction Microscopy", Ian Robinson and Jianwei Miao, Materials Science Bulletin 29 177-181 (2004)@footnote 4@"Coherent X-ray Diffraction from Quantum Dots", I. A. Vartaniants, I. K. Robinson, J. Onken, M. A. Pfeifer, G. J. Williams, F. Pfeiffer, T. H. Metzger, Z. Zhong and G. Bauer, Physical Review B 71 245302 (2005) .

**2:40pm SS1-TuA3 Binding Distances of Pi-conjugated Molecules on Cu(111) Studied by X-ray Standing Waves**, *A. Gerlach, F. Schreiber, S. Sellner,* Universität Tübingen, Germany*; N. Koch,* Humboldt University, Germany*; T.-L. Lee, J. Zegenhagen,* ESRF, France
Although the binding distances are very fundamental parameters, it is remarkable how little is known about these for most organic semiconductors on metal contacts. We study the adsorption of different aromatic molecules such as phthalocyanines, perylene derivatives, and oligoacenes on Cu(111) using the X-ray standing wave (XSW) technique. Element specific structural information of high precision is derived from the analysis of XSW yield measurements. Using the C(1s), N(1s), and F(1s) photoelectron signals we show that the molecules adsorb in a lying-down configuration, but with different distances relative to the metal substrate. The binding distances between the aromatic ring structure and the metal substrate are generally found to be larger than covalent bond lengths. Furthermore, we discuss more subtle effects as e.g. deformations@footnote 1@ of the adsorbed molecules that are related to the charge (re)distribution at the interface, which can be discussed in terms of rehybridization. Finally, we discuss recent attempts to determine the bending of aromatic ring structures based on chemical shift in the XPS signal. @FootnoteText@ @footnote 1@ A. Gerlach et al, Phys. Rev. B 71 (2005) 205425.

**3:00pm SS1-TuA4 Surface Segregation in a Polycrystalline Palladium-Copper Alloy**, *J.B. Miller*, *P. Ye,* Carnegie Mellon University*; C. Matranga,* U.S. Dept. of Energy*; A.J. Gellman,* Carnegie Mellon University
The surface composition of an alloy is rarely the same as its bulk. The differences are reflected in a number of important surface properties, including corrosion rates and catalytic activity. This work addresses the phenomenon of surface segregation in a polycrystalline palladium-copper alloy. Palladium-copper is of significant practical interest because of its potential as a hydrogen separation membrane for corrosive environments, like those found in coal gasification process streams. We combine X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS) techniques to understand how the compositions of the surface region (SR, ~ top 3-4 atomic layers) and top layer (TL) of a bulk 70:30 (atomic) Pd:Cu alloy vary with thermal treatment and adsorption of hydrogen sulfide. On the clean surface, copper enrichment, both in the SR relative to the bulk and in the TL relative to the SR, occurs at all temperatures above 600K. Adsorption of sulfur as hydrogen sulfide results in a palladium-only TL, illustrating how the presence of an adatom can significantly affect segregation patterns. We consider our results from the perspective of thermodynamic theory, and demonstrate that consideration of the heat of mixing is important for a complete description of this system.

**3:20pm SS1-TuA5 Sub-monolayer Sn/Cu(001) and Sn/Si/Cu(001) Structures**, *J. Lallo, L.V. Goncharova, B.J. Hinch*, S. Rangan, R.A. Bartynski, Rutgers University*; D. Strongin,* Temple University
Studies of Sn metal films on copper have been undertaken, as part of a wider program in understanding the thermal stability of Sn, and Sn with Si, films on copper surfaces. This STM investigation is motivated by the promoter effects of Sn in dichloro-dimethyl-silane production from Si/Cu catalysts. Four periodic superstructures, with sub-monolayer tin films grown at room temperature, have been seen with LEED. Comparatively recently, helium atom scattering (HAS) studies@footnote 1@ have also identified a 5@super th@ room temperature phase. While one STM identified phase has been previously reported,@footnote 2@ in this presentation we will show images of each of the known phases, and of surfaces supporting co-existing phases. Auger Electron Spectroscopy (AES) is used to establish relative Sn coverages, and to correlate the STM images with previously reported LEED and He diffraction data. We propose atomic structures for each of the stable room temperature Sn/Cu(001) phases. We also report on the thermal stability of these phases. At least one additional phase is produced only on annealing to 450K. Finally we present data on an ordered ternary Sn /Si /Cu(001) phase, and discuss the thermal stability of this phase also. @FootnoteText@ @footnote 1@L. Goncharova, Ph.D. Thesis, May 2003, Chemistry; Rutgers, The State University of New Jersey.@footnote 2@A.A. Cafolla, E. McLoughlin, Surface Science 544 (2003) 121-133.

**3:40pm SS1-TuA6 Epitaxial Growth of Gd Silicide Nanostructures on Si(001)**, *G. Ye, M.A. Crimp,* Michigan State University*; J. Nogami,* University of Toronto, Canada
Self-assembled gadolinium disilicide nanostructures grown on Si(001) substrates have been studied by scanning tunneling microscopy, transmission electron microscopy and atomic force microscopy. The nanostructures can be divided into two classes: highly elongated nanowires with hexagonal crystal structure and compact, rectangular islands with orthorhombic (or tetragonal) crystal structure. The different polymorphs of $GdSi_2$ have slightly different lattice parameters, and the nanostructure morphology is correlated with the magnitude and the direction of the silicide lattice mismatch with respect to the substrate. Different crystal structures can coexist within a single nanostructure, and the microscopy suggests that this is a result of phase transformation rather than coalescence. Possible mechanisms for this transformation are discussed. These results will be compared with similar data from Dy, Tb, and Sc silicide nanostructures to further reinforce the relationship between nanostructure morphology and crystal structure in these systems.

**4:00pm SS1-TuA7 Impact of Intrinsic Vacancy Ordering on Nanoscale Morphology and Structure: (Group-III)@subx@Se@suby@ on Si(111)**, *C.Y. LU, T.C. Lovejoy, M.A. Olmstead, F.S. Ohuchi,* University of Washington
Group III-Selenide semiconductors, where III=Al, Ga and In, are both structurally and chemically compatible with silicon, and have potential applications for spintronics and phase change memory devices. They crystallize a variety of bulk structures that incorporate intrinsic vacancies, including layered, defected zinc-blende, and defected wurtzite. Heteroepitaxy allows control of nanostructure morphology by inducing different arrangements of intrinsic vacancies. We report here an in-situ study using scanning tunneling microscopy and photoelectron spectroscopy to elucidate the role of intrinsic vacancies when Group III-Se films are grown on Si(111). Growth of Al@subx@Se@suby@ starts with a stable AlSe bilayer, followed by growth of Al@sub2@Se@sub3@, which forms triangle islands with edges aligned to  directions of Si(111), consistent with wurtzite Al@sub2@Se@sub3@ (helical vacancy structure). Ga@subx@Se@suby@ also starts with a stable interface bilayer (GaSe), but subsequent growth is layered Ga@sub2@Se@sub2@, with intrinsic vacancies in planes between the layers. For In@subx@Se@suby@, a stable InSe bilayer is not formed. Rather, it keeps the 7x7 substrate registry intact, eventually wetting the surface to form a flat morphology with ~10 nm ~hexagonal domains separated by misfit dislocations, consistent with crystalline @alpha@-In@sub2@Se@sub3@. This is despite the +4% lattice mismatch that might be expected to lead to 3-D island formation.

**4:20pm SS1-TuA8 Anisotropy in the Continuum Step Model: From Step Stiffness to Step-Edge Mobility\***, *T.J. Stasevich*, C. Tao, E.D. Williams, T.L. Einstein, University of Maryland

The evolution of vicinal surfaces can be efficiently simulated using the continuum step model.@footnote 1@ An important model parameter is the step stiffness, which quantifies how easily a step fluctuates and responds to driving forces. Due to the underlying crystal structure of vicinal surfaces, the stiffness can depend sensitively on step orientation, especially at temperatures low compared to the surface roughening transition (for noble metals, room temperature is considered low). Analytically accounting for this anisotropy within a lattice-gas framework is challenging, making direct comparisons with experiment or implementation in simulations time-consuming and computationally demanding. In this talk, we discuss simple, low-temperature approximations for the stiffness anisotropy on both {001} and {111} surfaces.@footnote 2@ These approximations only fail for steps aligned close to the high-symmetry direction, where an exact, explicit solution can fortunately be obtained. We exploit this by combining our simple formulas with small-angle expansions of the high-symmetry solutions, producing explicit, analytic approximations for the full anisotropy of step stiffness, accurate at nearly all experimentally relevant temperatures. We have recently implemented our formulas into finite-element simulations of the continuum step model. To make contact with experiment, we simulate the relaxation of a Ag(111) step initially pinned by surface impurities. By STM scanning, one pinning point was removed, and the step was thereafter observed to relax to a more favorable configuration. Matching our simulation to the experiment allows us to extract information about the adatom step-edge mobility,@footnote 3@ a parameter traditionally difficult to isolate. @FootnoteText@ *Work supported by NSF-MRSEC at UMD.@footnote 1@Jeong and Williams, Surf. Sci. Rep. 34, 171 (1999).@footnote 2@Stasevich et al., PRB 70, 245404 (2004) and PRB 71, 245414 (2005).@footnote 3@Tao et al., PRB 73, 125436 (2006).

**4:40pm SS1-TuA9 Argon Beam Mediated Modification of Nanotube-Based Structures using Classical Molecular Dynamics**, *S.K. Pregler*, S.B. Sinnott, University of Florida

Argon deposition on polymer and nanostructured carbon substrates can induce localized surface chemical modifications that include cross-linking and chemical functionalization. Here, we examine argon deposition at 80 eV on graphite sheets, multi-walled carbon nanotubes, and polymer-carbon nanotube composites at experimentally relevant fluences. The approach is classical molecular dynamics simulations using the reactive empirical bond-order (REBO) potential to determine the interactions for short-ranged interactions and the Lennard-Jones potential to determine the forces for long-ranged interactions in the multi-walled carbon nanotube and nanotube-polymer composite systems. The graphite system is modeled with the adaptive intermolecular REBO (AIREBO) potential. Several types of defects are predicted to occur in the graphite system, and they show good agreement with experimental findings. In the case of the multi-walled carbon nanotube system, the influence of deposition on the mechanical properties of the nanotube (sword-in-sheath failure) is shown to be considerable. Lastly, the argon beam is predicted to cause substantial changes to the interfaces in the nanotube-polymer composite systems. This work is supported by the National Science Foundation (CHE-0200838).

## Surface Science
## Room 2004 - Session SS2-TuA

### Water-Surface Interactions on Metals
**Moderator:** B.D. Kay, Pacific Northwest National Laboratory

**2:40pm SS2-TuA3 Wetting on Metal Surfaces at Ambient Conditions: A Photoemission Spectroscopy Study**, *S. Yamamoto*, K. Andersson, Stanford Synchrotron Radiation Laboratory; H. Bluhm, G. Ketteler, D.E. Starr, Lawrence Berkeley National Laboratory; T. Schiros, Stanford Synchrotron Radiation Laboratory; M. Salmeron, Lawrence Berkeley National Laboratory; H. Ogasawara, A. Nilsson, Stanford Synchrotron Radiation Laboratory

The wetting phenomena at surfaces play a crucial role in chemical, biological and environmental processes, such as heterogeneous catalysis, corrosion and the global cycling of chemical elements. The structure and property of water on surfaces in equilibrium with its vapor at ambient conditions, however, remains poorly understood. Here we have investigated the adsorption of water on Cu(110) and Cu(111) at ambient conditions (T= 0~200 @super o@C, relative humidity< 25 %), using in-situ X-ray photoemission spectroscopy. Cu(110) and (111) surfaces exhibit a remarkable difference in the wettability and water chemistry. On Cu(110), the OH and H@sub 2@O mixed layer is observed at relative humidities below 0.1 % (wetting). In contrast, on Cu(111), neither hydroxyl species nor molecular water are present even at a relative humidity of 25 % (non-wetting). This difference originates from the activation barrier for water dissociation on two Cu surfaces ((111)>(110)). Once the hydroxyl groups are formed on the surface, they act as anchoring sites for water molecules. This is because the hydrogen bond between OH and H@sub 2@O is stronger than that between two water molecules. We will also show that the wettability of surfaces can be controlled by preadsorbed oxygens, which change the dissociation barrier of water.

**3:00pm SS2-TuA4 Water Clusters Growth on Pd(111) and Ru(0001) Studied by STM**, *M. Tatarkhanov*, E. Fomin, University of California at Berkeley; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

Water clusters formation on clean Pd(111) and Ru(0001) surfaces has been studied using home-built variable temperature ultra-high vacuum scanning tunneling microscopy. Clusters with honeycomb internal structure were formed after low coverage and low temperature adsorption. Increasing the coverage of water at low temperature doesnâ?Tt create complete monolayer on both Pd(111) and Ru(0001), water forms very dense clusters and then starts to form second layer. This double layer exists only below 140K temperatures, after which it transforms into elongated clusters with bright perimeter for increased temperatures.

**3:20pm SS2-TuA5 Effect of Oxygen on the Structure and Dissociation of Water on Ru(0001)**, *A. Mugarza*, Lawrence Berkeley National Laboratory and Institut de Ciencia de Materials de Barcelona, Spain, US; T.K. Shimizu[1], Lawrence Berkeley National Laboratory; J. Cerda, Instituto de Ciencia de Materiales de Madrid CSIC, Spain; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

The adsorption and dissociation of water on Ru(0001) with 0.03 ML of pre-adsorbed O has been studied as a function of temperature by scanning tunneling microscopy. Below 140 K and at very low coverage (0.004 ML) water form complexes with O as well as dimer and trimer aggregates. At higher coverage (0.012ML) in this temperature range larger clusters with visible internal structure are observed. After annealing to 140 K, extended chain (worm-like) structures with enhanced contrast at the periphery are observed. By comparing the experimental images with theoretical calculations these structures have been attributed to mixtures of H@sub2@O and OH. The presence of O lowers the onset temperature for partial dissociation of water and affects the shape and internal structure of the clusters. In addition, atomic O reacts with the H on the surface to form OH. As the annealing temperature is raised to 220 K the worm-like structures disappear while, the concentration of H and OH increase, giving rise gradually to the formation of 2x2 O islands. These observations will be discussed and compared to the structures found on clean Ru(0001).

**3:40pm SS2-TuA6 The True Ground State of Water Adlayers on Ru(0001)**, F. Traeger, D. Langenberg, *C. Wöll*, Ruhr-Universitat Bochum, Germany

Recently the structure of water adlayers adsorbed on Ru(0001) has given rise to a pronounced controversy.@footnote 1-5@ One reason for the ongoing debate are experimental problems arising from the fact that H2O-adlayers on this surface exhibit a very low threshold for electron beam damage. Here we present the first results on the structure of water (D2O) adlayers on Ru obtained with a method where electron beam damage (either through primary or secondary electrons) can be strictly excluded. Results from He-atom scattering (HAS) reveal that the true ground-state of water on this surface exhibits a high-order commensurate structure. The HAS diffraction patterns are not consistent with any of the previous structural models proposed for this adsorbate system, either on the basis of experimental results or theoretical investigations. Test experiments revealed that the water adsorbate is indeed very sensitive to electrons, even short exposure times in front of the LEED instrument led to the formation of the well-known (R3xR3)R30Â° structure.@footnote 1@ HAS measurements also demonstrate that electron irradiation results in both, electron induced desorption and electron-induced dissociation. We have developed an optimized preparation procedure for high-quality water adlayers, which is somewhat different from the previously proposed procedure. Structural models for the true ground state of water on the Ru(0001)-surface will be presented in the talk. @FootnoteText@ @footnote 1@ G. Held and D. Menzel, Surf. Sci. 316, 92, (1994).@footnote

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

2@ P. J. Feibelman, Science 295, 99, (2002).@footnote 3@ C. Clay, S. Haq and A. Hodgson, Chem. Phys. Lett. 388, 89, (2004).@footnote 4@ K. Andersson et al., Phys. Rev. Lett. 93, 196101-1, (2004).@footnote 5@ J. Weissenrieder et al., Phys. Rev. Lett. 93, 196102-1, (2004) .

**4:00pm SS2-TuA7 Wetting and Multilayer Growth on Metal Surfaces**, *A. Hodgson, G. Zimbitas, M. Gallagher, S. Haq, G.R. Darling,* The University of Liverpool, UK

We describe the wetting behaviour of water ice films on Ru(0001) and Pt(111) and how this is modified by OH co-adsorption. Both metals will form an intact water monolayer, but with different structures and wetting behaviour. Water forms a labile wetting layer on Pt(111), with hexagonal @sr@37 and @sr@39 ice structures at increasing coverage. Multilayer adsorption forms clusters whose size and registry to the @sr@39 layer depends on thickness and preparation conditions, thick ice films forming an oriented incommensurate crystalline ice, stabilised by reconstruction of the interface layer. OH co-adsorption pins the wetting layer into registry with Pt, forming an ordered (OH+H@sub 2@O) phase which can not restructure in response to multilayer adsorption. Although this layer has a similar OH@sub x@ skeleton to ice Ih, water does not form a stable 2D wetting layer and the surface is hydrophobic. On Ru(0001) the strong water-metal interaction pins the first monolayer into a structure that is unfavourable for hydrogen-bonding to a multilayer ice film. This layer does not wet, even for thick films, instead thick 3D multilayer ice clusters form which minimise their contact to the water monolayer. No ordered multilayer ice structure is formed, indicating that the tightly bound wetting layer does not reconstruct to accommodate the incommensurate ice Ih(0001) film to the metal surface. The factors influencing multilayer adsorption are examined using DFT calculations to compare adsorption on top of different water and (OH+H@sub 2@O) structures. We argue that wetting is determined by the ability of the first layer to restructure to optimise the bonding between a bulk ice layer and the metal surface.

**4:20pm SS2-TuA8 Adsorption and Desorption Kinetics on a Porous Solid: N@sub 2@ on Amorphous Solid Water**, *T. Zubkov,* Pacific Northwest National Laboratory*; T.R. Engstrom,* University of Texas at Austin*; R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Desorption of a weakly bound adsorbate from a porous solid was studied for the case of molecular nitrogen on amorphous solid water (ASW). Porous ASW films of different thickness were grown on Pt(111) by ballistic deposition. N@sub 2@ adsorption and desorption kinetics were monitored mass-spectrometrically. Temperature programmed desorption spectra show that with the increasing film thickness, the N@sub 2@ desorption peak systematically shifts to higher temperatures. The results are explained and quantitatively reproduced by a simple model, which assumes that the N@sub 2@ transport within the film is faster than the depletion rate to vacuum. The local coverage at the pore mouth determines the desorption rate. For thick ASW films (>1 µm), the assumption of the fast equilibration within the film is shown to be no longer valid due to diffusion limitations. The mechanisms of the adsorbate transport are discussed.* @FootnoteText@ *Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

## Thin Film
## Room 2022 - Session TF+SS-TuA

### Surface Functionalization for Selective Area ALD
**Moderator:** T.M. Klein, The University of Alabama

**2:00pm TF+SS-TuA1 Surface Functionalization for Selective Area ALD**, *R. Chen, J. Hong, **S.F. Bent,** Stanford University* **INVITED**

Atomic layer deposition (ALD) is a powerful ultra-thin film deposition method for preparing a variety of materials. Typically, the process permits nano-scale control of materials in the vertical direction. To develop the method for three-dimensional control of materials, we have been investigating an area-selective ALD technique which will enable micro- and ultimately nano-scale definition of the lateral structure. Our approach is to chemically modify the substrate surface in order to impart spatial selectivity to ALD. Our focus is on both oxide materials (e.g. HfO@sub 2@ and ZrO@sub 2@) and metals (e.g. Pt) deposited by ALD. We have investigated several different types of self-assembled monolayers (SAMs) as resists against ALD using both solution and vapor delivery methods. Oxide-coated substrates (e.g. SiO@sub 2@) have been protected using organosilane-based SAMs, and hydrogen-terminated Si and hydrogen-terminated Ge protected by reaction with alkenes or alkynes. We have

followed the SAM properties as a function of molecular structure and formation time using a variety of experimental techniques and have correlated the properties of the SAMs with their efficacy as ALD resists. With the successful ALD resists, area-selective ALD has been carried out using different patterning methods to define the lateral structure. Both microcontact printing of the SAMs and selective functionalization of a SiO@sub 2@/Si structure have been used to achieve area-selective ALD. We have compared the selectivity between the two methods, and will discuss the differences in the context of the SAM resist requirements. We will also show that by choosing either silylation- or hydrosilylation-based chemical functionalization, a single patterned oxide substrate can be used for either positive or negative pattern transfer into the ALD film.

**2:40pm TF+SS-TuA3 Surface Mechanisms in Oxygen-Based Noble Metal Atomic Layer Deposition**, *K.J. Park, S.M. Stewart, **G.N. Parsons,** North Carolina State University

Atomic layer deposition of noble metals, including Pt, Ru, Re, and Rh, is often achieved using a binary exposure sequence of metal-organic precursors and oxygen, and processes show saturation near one monolayer per growth cycle for varying oxygen exposure and for varying metal-organic exposure. The surface typically oxidizes during the oxygen exposure step, and then the metal precursor ligand is oxidized during the precursor exposure, leaving a single layer of metal deposited on the surface. We have recently observed that for the case of Ru ALD from bis-(cyclopentadienyl) ruthenium and oxygen, the growth thickness per cycle saturates at a value that depends on the extent of oxygen exposure in the ALD sequence. On-line Auger spectroscopy analysis shows that the extent of metal surface oxidation increases with the extent of oxygen exposure, suggesting that the extent of Ru ligand oxidation is determined by the amount of oxygen available at the surface. This is consistent with the observed increase in Ru film growth/cycle during the Ru(Cp)2 exposure step. This dependence of film growth/cycle on oxygen exposure can explain the previously observed pressure dependence of growth thickness per cycle during Ru deposition which is not expected in an ALD process. We believe these observations lead to new insights into methodologies to significantly expand and control the process window and nucleation in Ru ALD, and this can likely be extended to other noble metal ALD processes.

**3:00pm TF+SS-TuA4 Atomic Layer Deposition of Hafnium Silicate Gate Dielectric Layers**, *A. Delabie, G. Pourtois, M. Caymax, S. De Gendt, L.-A. Ragnarsson, M.M. Heyns,* IMEC, Belgium*; Y. Fedorenko, J. Swerts, J.M. Maes,* ASM Belgium* **INVITED**

Downscaling Equivalent Oxide Thickness (EOT) by decreasing the physical thickness or increasing the permittivity of the gate dielectric is required to reach the CMOS (sub) 45 nm node performance specifications. Hafnium silicate is widely investigated as a high-k gate dielectric due to its thermodynamic stability with silicon. In this work, we study the growth mechanism of hafnium silicate Atomic Layer Deposition (ALD) by combining experiment and theory. Thorough understanding of the ALD mechanisms can contribute to improved film quality and downscaling. The hafnium silicate reaction cycle consists of well separated precursor reactions in the sequence (H@sub 2@O/HfCl@sub 4@)@sub x@/(H@sub 2@O/X)@sub y@ with X a HfCl@sub 4@ compatible Si precursor.@footnote 1@ The composition of hafnium silicate is varied by adjusting x and y. Hafnium silicate films are characterized ex-situ by Rutherford Backscattering (RBS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOFSIMS) and X-Ray Photoelectron Spectroscopy (XPS). Electrical properties are evaluated on TaN gated capacitors. The interaction of ALD surface sites with the precursors is investigated by Density Functional Theory based calculations on cluster models. Our insight in the ALD reaction mechanism allows optimization of the hafnium silicate deposition, resulting in a leakage current reduction of one order of magnitude. @FootnoteText@ @footnote 1@ will be revealed at the conference .

**3:40pm TF+SS-TuA6 Mechanistic Details of TiN Atomic Layer Deposition (ALD) Processes**, *H. Tiznado, **F. Zaera,** University of California, Riverside

The reaction mechanisms of atomic layer deposition (ALD) processes have been characterized by a combination of surface sensitive techniques. In this talk our study of the deposition of TiN films from TiCl@sub 4@ and ammonia will be used to illustrate the power of this approach. First, each of the two half steps comprising the ALD process was studied independently. It was found that exposure of the surface to TiCl@sub 4@ leads to the initial deposition of titanium in the +3 oxidation state; only at a later stage most of it appears in the +4 state expected for TiCl@sub 4@. Also, the Cl:Ti final ratio at the end of the TiCl@sub 4@ deposition reaches a value of ~ 3.5, indicating some chlorine removal. Subsequent treatment with

ammonia removes most of the remaining Cl and deposits the required nitrogen, as expected. Nevertheless, some chlorine is still seen on the surface, most likely because of HCl readsorption. The buildup of thicker films was tested by performing multiple cycles with alternating exposures to $TiCl_4$ and $NH_3$. Similar films could be deposited on glass and on W, Ni and Cu foils. Interestingly, depth-profiling studies show that the resulting film consists of a $Ti_3N_4$ layer on top of TiN. This suggests that the reduction of titanium takes place during the exposure of the surface to $TiCl_4$, not $NH_3$, and that it is the first reaction of the cycle the rate limiting in the whole ALD process.

4:00pm **TF+SS-TuA7 Surface Processes of Plasma-Assisted Atomic Layer Deposition**, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands **INVITED**
Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with precise thickness control. The extension of the technique with plasma processes (i.e., plasma-assisted ALD) provides several potential advantages over thermal ALD such as an enhanced growth rate, improved material properties, and lower deposition temperature. However mechanistic studies are scarce and detailed insight into the surface processes of plasma-assisted ALD is still lacking while being imperative for further process optimization. In this contribution surface processes during plasma-assisted ALD are addressed on the basis of studies of oxide ($Al_2O_3$, $HfO_2$) and metal nitride (TiN, TaN) film growth employing several in situ diagnostics. From in situ spectroscopic ellipsometry and quartz crystal microbalance measurements precursor adsorption reactions are discussed addressing the formation of surface species, substrate-inhibited growth, and film nucleation. The surface reaction products as well as the consumption of precursor and plasma species are discussed from time-resolved mass spectrometry studies as well as from optical emission spectroscopy, a unique feature provided by the plasma process. On the basis of the results, the paradigms for plasma-assisted ALD are reviewed and differences with thermal ALD processes are discussed.

# Tuesday Evening Poster Sessions, November 14, 2006

## Surface Science
## Room 3rd Floor Lobby - Session SS-TuP

### Surface Science Poster Session

**SS-TuP1 Design and Stability of Surface Alloys used for Catalytic Conversion of Fossil Fuel to Hydrogen**, *J. Knudsen*[1], *R.T. Vang,* University of Aarhus, Denmark*; J. Schnadt,* Lund University, Sweden*; E.K. Vestergaard, T.M. Pedersen, B. Hammer, T. An, I. Stensgaard, E. Laegsgaard,* University of Aarhus, Denmark*; A.U. Nilekar, M. Mavrikakis,* University of Wisconsin-Madison*; F. Besenbacher,* University of Aarhus, Denmark

Clean, cheap and efficient production of high-purity hydrogen is an essential prerequisite for the emerging hydrogen economy. The vast majority of the present hydrogen production comes from catalytic conversion of fossil fuel, which relies heavily on the steam reforming (SR) reaction and the Water-Gas-Shift (WGS) reaction. Supported Ni particles are commercially used as catalysts for the SR reaction, whereas supported Cu particles are currently used for the low-temperature WGS reaction. In this study vacuum deposition of Cu onto Pt(111) at 800 K is used to synthesize stable near-surface alloys (NSA) of Cu/Pt(111). A combination of scanning tunneling microscopy (STM), Core-level photoemission (XPS), Thermal desorption spectroscopy (TDS) and Density functional theory (DFT) is used to characterize the NSAs, and it is found that Cu atoms are stabilized sub-surface, leaving a surface layer free of Cu atoms. Very interestingly, we find that the WGS activity of our new NSA is superior to that of Cu(111), and it is, therefore, very likely that real Cu/Pt near-surface particles could be used as new and improved catalysts for the WGS reaction. Finally, fast high-pressure STM experiments in a high CO pressure are used to examine the stability of this new Cu/Pt(111) near-surface alloy for the WGS reaction, and a previously found Au/Ni(111) surface alloy, which can be used for the SR reaction. From these experiments we conclude that the Cu/Pt(111) NSA remains stable in high pressure of CO in contrast to the Au/Ni(111) surface alloy, which is found to phase separate into small Au clusters on a Ni(111) substrate due to formation of Ni-carbonyls, which remove Ni from the surface.

**SS-TuP2 Vibrational Energy Flow in a Gas-Surface Reaction**, *D.R. Killelea*[2], *A.L. Utz,* Tufts University

Energy flow plays a central role in the activation of surface reactions. We measure how energy selectively deposited into the translational, rotational, and vibrational coordinates of methane influences $S_0$ on Ni(100) and Ni(111) to answer key questions about energy flow in this prototypical gas-surface reaction. Infrared laser excitation of $CH_4$ in a supersonic molecular beam prepares a microcanonical ensemble of reagents with well-defined internal and translational energies. We quantify reactivity for the state-selected reagents and observe non-statistical patterns of activation, including vibrational mode specificity. For example, the $\nu_3$ C-H stretch is more reactive than the second overtone of the umbrella-bending mode, $3\nu_4$, even though $3\nu_4$ contains 30% more energy. On Ni(111) energy deposited in $\nu_3$ activates dissociative chemisorption more than an equivalent amount of translational energy. To understand these results, we propose a framework for describing energy flow among the energetic degrees of freedom available to the molecule-surface reaction complex. Our model draws on and is consistent with descriptions of intramolecular vibrational energy flow in both the gas-phase and in liquids, but accounts for features unique to gas-surface reactivity. We focus on the characteristic timescales for energy flow and the molecule-surface interaction time. We conclude that for direct dissociative chemisorption of $CH_4$, there is insufficient time for full energy randomization among the energetic degrees of freedom in the molecule-surface reaction complex. Our model not only predicts vibrational mode-specific behavior - it also suggests a consistent explanation of surface temperature effects, explains the success of statistical theories to model ensemble-averaged reactivity even when energy flow is not statistical, and provides a framework for assessing the extent of energy flow in other gas-surface reactions.

**SS-TuP3 Unexpected Growth Modes for Heteroepitaxial $BaTiO_3$ Films Due to Kinetic Limitation**, *J. Shin*[3], The University of Tennessee; *A.Y. Borisevich, S.V. Kalinin,* Oak Ridge National Laboratory; *E.W. Plummer,* The University of Tennessee*; A.P. Baddorf,* Oak Ridge National Laboratory

Fully strained $BaTiO_3$ (BTO) films have the strongest polarization because the c/a ratio is maximized. However, epitaxial growth of BTO films on $SrTiO_3$ (STO) is very difficult in oxygen pressures above 1 mTorr due to a large lattice mismatch (2.28%) and the Stranski-Krastanov (SK) growth mode with lattice relaxation is likely. To avoid the formation of 3D islands and prevent the system from reaching equilibrium, kinetic limitations can be used to reduce the surface diffusion length by changing the growth rate or the growth temperature. BTO films grown on (001)STO substrates by pulsed laser deposition have been investigated as a function of growth temperature and growth rate by atomic force microscopy, x-ray diffraction, reflection high energy electron diffraction, and transmission electron microscopy (TEM). The 125 nm thick BTO films deposited using the relatively high average growth rate (0.2 ML/s) with 10 mTorr oxygen pressure exhibit layer-by-layer or layer-then pseudo 2D island growth modes with increasing temperature, which is also related to thermal expansion differences between films and substrate. Compared with low growth rate (0.08 ML/s) condition, which shows conventional SK growth above 1 mTorr oxygen, this high growth rate condition provides 125 nm thick BTO films that are highly strained with visible terraces. In addition to the conventional layer-by-layer mode, an unusual pseudo 2D island growth mode is observed above 1050 K, where islands of several unit cell heights are observed between single height film steps. These islands are nearly steady-state; once formed, the film roughness does not increase with thickness as it does for 3D islands, and the island size and density remains fixed, with evidence of island-island repulsion. Pseudo 2D island growth appears related to the lattice of film dislocations observed with TEM. Research sponsored by Office of BES, U.S. DOE, under contract DE-AC05-00OR22725 with ORNL, managed by UT-Battelle, LLC.

**SS-TuP4 Partially Dissociated Water Clusters on Ru(0001) Studied by Scanning Tunneling Microscopy**, *T.K. Shimizu,* Lawrence Berkeley National Laboratory and University of California at Berkeley*; A. Mugarza,* Lawrence Berkeley National Laboratory and Institut de Ciencia de Materials de Barcelona, Spain, US*; J. Cerda,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

Individual molecules in partially dissociated water clusters have been imaged at 6K using a home-built low temperature scanning tunneling microscope (STM). After annealing the surface with pre-adsorbed oxygen and water above 140 K, elongated clusters with enhanced contrast at the perimeter were observed. By comparing the experimental data with STM simulations, we conclude that the clusters consist of mixed water and hydroxyl molecules lying flat. The presence of pre-adsorbed oxygen prevents the formation of a perfect hexagonal network inside the clusters and affects their overall shapes. Hydrogen atoms were observed both inside and outside the clusters, the latter reacting with the pre-adsorbed oxygen to form hydroxyl.

**SS-TuP5 Gold Adatom-mediated Bonding in Self-assembly of Alkanethiols on the Au(111) Surface**, *P. Maksymovych*[4], University of Pittsburgh*; D.C. Sorescu,* U. S. Department of Energy*; J.T. Yates, Jr.,* University of Pittsburgh

The majority of self-assembled molecular monolayers (SAMs) are at present grown using the adsorption of alkanethiol molecules on the Au(111) surface. Despite decades of research in this field, the structural nature of the S-Au anchor bond of the thiolate to the Au(111) surface is still a matter of active debate. We addressed this issue by studying the decomposition of prototypical $CH_3SH$, $CH_3SSCH_3$ and $C_3H_7SH$ molecules on the Au(111) surface using Scanning Tunneling Microscopy (STM) and Density Functional Theory. Initially, the $CH_3S$ species were produced by STM-tip induced dissociation of $CH_3SH$ or $CH_3SSCH_3$ molecules on the Au(111) surface at 5K. By comparing the experimental and calculated STM images of the $CH_3S$ species produced in this way, we determined that the S-headgroup adsorbs on the two-fold coordinated bridge-site between two surface Au atoms, consistent with theoretical predictions for this system. In the next step, $CH_3SSCH_3$, $CH_3SH$ and $C_3H_7SH$ molecules were dissociated thermally in conditions typically used for SAM growth. Unexpectedly, we

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find that dissociation of the parent molecules in these conditions is mediated by gold adatoms, which populate the Au(111) surface at elevated temperatures. The product CH@sub 3@S (and C@sub 3@H@sub 7@S) species form self-assembled Au adatom-bound complexes, which have substantially higher calculated binding energy than CH@sub 3@S species bonded to the Au(111) surface. The involvement of Au adatoms in the self-assembly of alkanethiols resolves the current controversy around the headgroup-sulfur bonding, as we show for the case of the low-coverage stripe-phase SAM, and explains the morphological changes of the Au(111) surface that accompany self-assembly. We thank W. M. Keck Foundation and NEDO (Japan) for the financial support of this work.

**SS-TuP6 Heterogeneous Oxidation of the Si(111) Surface Determined by Kelvin Probe Force Microscopy**, *B Poelsema*, J.M. Sturm, G.O. Croes, University of Twente, The Netherlands; *H. Wormeester,* University of Twente, The Netherlands, Netherlands

A large change in work-function occurs during the initial oxidation of Si(111). The variation of the work-function after an initial exposure to O@sub 2@ allows the identification of a molecular precursor. An AFM with a conducting tip has been used as a Kelvin Probe Force Microscope (KPFM). It enables the in-situ, parallel recording of morphology and work-function with nanometer resolution. The clean Si(111) surface has been found to have a rms work-function variation of only 2 meV, indicative of an electrically very smooth surface. Exposure to molecular oxygen results in a very heterogeneous oxidation process in which morphology and work-function locally change in a non-correlated fashion. After an exposure of about 10 L(angmuir), the morphology remains similar, while over 100 L is required for the work-function to assume a stationary value. The change in work-function is only local as the average value is constant after 40 L and the rms of the work-function does not significantly change after 20 L. The heterogeneity of the oxidation process is also observed by a strong variation of the differential capacitance over the surface. This variation is strongly correlated to the local morphology indicating a large variation in local oxide thickness. The observations above can be rationalized via the presence of a molecular precursor. It actually has strong effects at sub-monolayer coverage.

**SS-TuP7 Initial Oxidation Process of Si(100) Surface with O@sub 3@ Molecular Beam**, *I. Kinefuchi,* The University of Tokyo, Japan; *H. Yamaguchi,* Nagoya University, Japan; *Y. Sakiyama, S. Takagi, Y. Matsumoto,* The University of Tokyo, Japan

The reaction of O@sub 3@ with Si(100) surface has been investigated by employing molecular beam techniques. The surfaces were oxidized at 673 K by exposure to 5.1%-O@sub 3@/O@sub 2@ beam and we examined the decomposition of the oxide adlayers using temperature programmed desorption (TPD). Compared with O@sub 2@, O@sub 3@ significantly enhances the oxidation rate in the low coverage regime. The coverage-exposure relationship up to 2.8 monolayers in thickness follows the modified Langmuirian kinetics, where the initial sticking probability of O@sub 3@ is almost unity. The desorption spectra exhibit higher peak temperatures and narrower distributions than those from the adlayers by pure O@sub 2@ beam. The surface adlayers formed with O@sub 3@ therefore have more stable and less heterogeneous structures than those formed with O@sub 2@. We also employed the molecular beam reactive scattering (MBRS) technique to investigate the reaction dynamics of the active oxidation process. The square-wave modulated beam of high concentrated O@sub 3@ gas (~60%-O@sub 3@/O@sub 2@ diluted with He) was directed to the surface at temperatures between 1033 and 1153 K. The surface transfer function shows that the reaction process is a sequential two-step first-order reaction as observed with O@sub 2@ beam. However, the reaction rate of the first step, which corresponds to the formation of the desorption precursor, is at least two times faster than that with O@sub 2@. This suggests that there is another reaction pathway involving atomic oxygen due to the decomposition of O@sub 3@ on the surface. @FootnoteText@ @footnote 1@ One of the authors (I.K.) was supported through the 21st Century COE Program, "Mechanical Systems Innovation," by the Ministry of Education, Culture, Sports, Science and Technology.

**SS-TuP8 Temperature Dependant Evolution of Co Islands on Ag/Si(111)-@sr@3x@sr@3and Ag/Ge(111)-@sr@3x@sr@3**, *S.L. Tsay,* National Taiwan Normal University; *C.L. Lin,* Academia Sinica of China; *T.Y. Fu,* National Taiwan Normal University

Thermal evolution of Co islands on Ag/Ge(111) and Ag/Si(111) surfaces was studied by scanning tunneling microscopy and low energy electron diffraction. The Ag buffer layer with @sr@3x@sr@3 reconstruction can avoid alloy formation of Co and Ge or Si during annealing below 800K. The morphology of 0.35ML Co on the Ag/Ge(111) surface transfers dispersion of clusters to nucleation of 2D islands. The 2D islands with @sr@13x@sr@13R14° reconstruction form after 573K annealing. Anneal to above 573K, the 2D islands grow up and the higher islands are reconstructed by 2x2. Submonolayer Co on Ag/Si(111) surfaces can not form 2D islands. The Co clusters just become larger as annealing temperature increases. However, 2x2 phase can be found on 1.8ML Co/Ag/Si(111) surfaces after 673K annealing. The different growth behaviors of Co atoms on Ag/Si(111) and Ge(111) surfaces are discussed from different structure factors.

**SS-TuP9 Neutralization and Ionization during Impact of Low Energy Si@super +@ with Surfaces**, *X. Chen,* Z. Sroubek, J.A. Yarmoff, University of California, Riverside

The interaction of low energy semiconductor ions with solid surfaces has been largely unexplored. In this work, 1-5 keV Si@super +@ ions are used to induce direct recoil (DR) from Al(100) and Si(111), and are scattered from electropositive and electronegative adatoms adsorbed on these surfaces. In the DR experiments, significant yields of fast, monoenergetic doubly and triply charged Al and Si ions are produced, which is in contrast to the secondaries formed during bombardment by noble gas ions. The Al@super 2+@ and Al@super 3+@ are attributed to an efficient promotion of Al 2p level during the electronically nearly-symmetric Si-Al collision, and subsequent shake-off processes. The yield of triply charged ions in DR from Si is reduced from that of Al, due to the more symmetric electronic structure. Si@super +@ ions were backscattered from submonolayers of Cs and I deposited onto Al(100) and Si(111). Because of the high ionization energy of Si, resonant charge transfer would be expected to completely neutralize the scattered projectiles. A considerable fraction of the Si backscatters from the adatoms as positive and negative ions, however. Mechanisms responsible for the ion formation will be discussed.

**SS-TuP10 Running Current through a Single Non Resonant Quantum State in Silicon**, *M. Berthe, A. Urbieta, R. Stiufiuc, B. Grandidier, D. Deresmes, C. Delerue, D. Stievenard,* Institut d'Electronique, de Microelectronique et de Nanotechnologie, France; *R. Rurali, N. Lorente,* LCAR (UMR 5589), France; *L. Magaud,* Laboratoire d'Etude des Proprietes Electronique des Solides (LEPES-CNRS), France; *P. Ordejon,* Institut de Ciencia de Materials de Barcelona, Spain

Due to its ability to resolve geometric structures on the atomic scale, scanning tunnelling microscopy (STM) is a technique well suited to identify individual point defects on a surface. In principle, its versatility should allow to spectroscopically characterize the coupling of tunnelling electrons to the electronic states and the nuclear motions of a defect. Such a measurement, which has recently been achieved on isolated molecules adsorbed on a thin insulating layer still needs to be demonstrated for other systems, particularly semiconductor systems. We have studied the transfer of electrons through the localized dangling bond state of an isolated Si adatom lying in a passivated silicon surface at 5 Kelvin. While the state is electronically decoupled from the silicon bulk states, a strong electron-vibration coupling is evidenced by measurement of the inelastic current and supported by density functional calculations.

**SS-TuP11 Valence-Band and Core-Level X-Ray Photoelectron Spectroscopy of Lead Sulfide Nanocrystal/Polymer Composites**, *D.J. Asunskis,* L. Hanley, University of Illinois at Chicago

Lead salt nanocrystals have been the subject of intense recent interest due to their potential applications in photovoltaics, near infrared sensors, and other optoelectronic devices. However, relatively few studies have used photoemission to probe the electronic structure of these novel nanomaterials. Valence-band and core-level X-ray photoelectron spectroscopy (XPS) are therefore used to probe different lead sulfide (PbS) nanocrystal-polymer nanocomposites. Composite materials are prepared by trapping monodisperse 3 and 10 nm lead sulfide nanocrystals in two polymers, the non-conducting polymer, polystyrene, and the conjugated polymer, poly (2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene or MEH-PPV. Additional composites with polydisperse lead sulfide nanocrystals were synthesized by growing the particles in the presence of MEH-PPV and poly (vinyl alcohol). These materials are initially characterized by UV/Vis optical absorption and transmission electron microscopy to monitor the particle size in the composites. Monochromatic XPS with charge neutralization is then used to collect both core-level and valence-band spectra. The composites with monodisperse particle sizes exhibit a shift to lower energy of the highest occupied molecular orbital as the lead sulfide particle size increases from 3 to 10 nm. Oxidation of the

sulfur content in the particles by air during fabrication and transport was minimal as evident by the small contribution of oxidized sulfur in the XPS spectra. The core level XPS results also show additional states in the lead core XPS regions that change as the particle size changes. The monodisperse composites are compared to the other composites synthesized having varied particle size, showing the effects of size variance and polymer/particle bonding in the core level and valence band XPS spectra.@footnote 1@ @FootnoteText@ @footnote 1@This work is supported by the U.S. Department of Defense.

**SS-TuP13 Isocyanate and Isothiocyanate Reactions at the Ge(100)-2x1 Surface**, *P.W. Loscutoff*, *S.F. Bent,* Stanford University

Recently, multiple layer deposition of organic molecules was demonstrated using the highly reactive isocyanate moiety. Continuing this work, we have studied the reactions of several isocyanates and isothiocyanates on the Ge(100)-2x1 surface using multiple internal reflection Fourier transform infrared spectroscopy. Results for phenyl isocyanate indicate that the molecule adsorbs as a [2+2] reaction product between the C=N of the isocyanate group and the Ge surface dimer, in agreement with the published reaction product for 1,4-phenylene diisocyanate. Adsorption studies of mono-isothiocyanates suggest the presence of a sulfur dative-bonded state as well as a cycloaddition product between the isothiocyanate group and the Ge dimer. The adsorption product for 1,4-phenylene diisothiocyanate also differs from that of the isocyanate analog, 1,4-phenylene diisocyanate, and appears to be adsorbing as a [3+2] reaction product. Nonetheless, the spectra show that there is an intact isothiocyanate moiety present in the adsorbed product, indicating the potential for a multiple layer reaction scheme. Future work includes reacting this intact isothiocyanate moiety with ethylene diamine to construct ultra thin films by molecular layer deposition, as well as utilizing X-ray photoelectron spectroscopy to further characterize the nature of isothiocyanate bonding at the Ge(100)-2x1 surface.

**SS-TuP14 Surface Characterization of Indium Nitride Layers Grown by High Pressure Chemical Vapor Deposition**, *R.P. Bhatta*, *B.D. Thoms, M. Alveli, N. Dietz,* Georgia State University

The growth of InN is difficult due to its low dissociation temperature and the high vapor pressure of nitrogen. High pressure chemical vapor deposition (HPCVD) was developed to overcome these challenges in InN growth. InN layers grown by HPCVD have been studied using several surface sensitive techniques. The InN surface was prepared by a combination of sputtering and atomic hydrogen cleaning (AHC). Auger electron spectroscopy and high resolution electron energy loss spectroscopy (HREELS) showed that AHC alone removes most surface contaminants but that some carbon remains. Argon ion sputtering was used to remove the residual carbon. Following sputter cleaning, AHC at 600 K restores surface order as demonstrated by 1x1 hexagonal low energy electron diffraction pattern. HREEL spectra of the atomic hydrogen cleaned layer show a Fuch-Kliewer surface phonon at 560 cm@super -1@ and adsorbate loss peaks at 3260 and 870 cm@super -1@ assigned to N-H stretching and bending vibrations, respectively. These assignments are confirmed by isotopic shifts using deuterium. No surface In-H vibrations are observed indicating the surface is terminated by N-H species and that the InN layer is N-polar. HREEL spectra also showed loss features due to conduction band plasmon excitations. The plasmon excitation shifted towards higher energy as the incident electron energy was decreased implying a higher plasma frequency at the surface than in the bulk, which in turn implies a surface electron accumulation layer. Electron energy loss spectroscopy in the energy range for electronic excitations was used to investigate the surface electronic structure.

**SS-TuP15 Etching of Si(100)-(2x1) with Cl under Super-Saturated Conditions: A Novel Reaction Pathway**, *A. Agrawal*, *R.E. Butera, J.H. Weaver,* University of Illinois at Urbana-Champaign

We investigated the consequences of Cl uptake beyond "saturation" on Si(100)-(2x1), and we discovered a new etching pathway. Si(100)-(2x1) surfaces that were saturated with Cl and had one adatom per dangling bond were exposed to a constant flux of Cl@sub 2@ in the temperature range of 750-850 K. They were then imaged at room temperature with atomic resolution scanning tunneling microscopy. We found that additional Cl can be accommodated via insertion in the Si-Si dimer bond or backbond to produce a super-saturated surface. This allowed the surface to evolve along a novel and previously unobserved etching pathway. Isolated dangling bonds created on the surface by phonon-assisted electron-stimulated desorption (PAESD) of Cl act as mediators for the insertion process. An abstraction reaction to re-saturate the dangling bond with Cl

dissociates the incoming Cl@sub 2@ to produce atomic Cl on the surface, which then inserts. SiCl@sub 2@ desorption from the super-saturated surface leads to etching that produces pits elongated along the dimer row direction. The rate limiting step in the etching process is the Cl insertion via the PAESD controlled dangling bond creation. The energetics of the etching process and the sequence of events leading to it will be presented.

**SS-TuP16 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@sub 2@ on Si(114) has been studied at room temperature using scanning tunneling microscopy. The three distinct structural units of the clean Si(114) surface (monomer, dimer, and tetramer) make it an ideal template to study the selective adsorption of a reactive species on a semiconductor surface. A mild anneal to 400-500 K following Cl@sub 2@ exposure allows the adsorbed Cl to interrogate the surface to find the most energetically favored adsorption site. With increasing exposure, Cl adsorbs on the monomer (@theta@@sub Cl@ @<=@ 0.25 ML), then the dimer (0.25 ML @<=@ @theta@@sub Cl@ @<=@ 0.50 ML), and finally the tetramer (@theta@@sub Cl@ > 0.50 ML). The difference in reactivity is attributed to @pi@ bonds within the dimer and tetramer units but not along the monomer row. The low reactivity of the tetramers reflects the presence of a @pi@-bonded ring-like structure composed of single @pi@ bonds along each of the tetramer arms as well as between the tetramer bridge. The adsorption of Cl removes the buckling of each surface unit transforming the surface from a mixed (2x1)-c(2x2) phase to a complete (2x1) phase at @theta@@sub Cl@ = 1 ML.

**SS-TuP17 Thermal and Non-Thermal Decomposition of Diethylamine on Si(100)**, *S. Yeninas*, *A. Brickman, J.H. Craig, Jr., J. Lozano,* Bradley University

Electron stimulated desorption (ESD), temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and high resolution electron energy loss spectroscopy (HREELS) were used to investigate the decomposition of diethylamine (DEA) on Si(100) surfaces. Adsorption of DEA on the silicon surface was studied by XPS and UPS. Changes in the valence band structure of silicon due to adsorption of DEA will be discussed. HREELS and TPD show carbon is thermally removed from the surface with the ethyl groups via a beta-hydride elimination process. TPD provides evidence that ethylene thermally desorbs from the substrate from two adsorbate states (at 560K and 760K) while methyl groups are desorb from only one state (560K). Non-thermal decomposition of DEA was studied by irradiating the surface with 600-eV electrons at 100K. TPD and HREELS data indicates decomposition of the parent molecule upon irradiation. After electron irradiation, TPD shows desorption of ethyl groups from only one adsorbate state. XPS data showed deposition of carbon and nitrogen and possible formation of nitrides and carbides on the surface after electron irradiation that could not be thermally removed.

**SS-TuP18 Dynamic Hydrophobicity on Ultrasmooth Alkyl and Fluoroalkyl Silanes Self-Assembled Monolayer Surfaces**, *N. Yoshida*, Kanagawa Academy of Science and Technology, Japan*; S. Suzuki,* Tokyo Institute of Technology, Japan*; M. Sakai, J.-H. Song, A. Hashimoto,* Kanagawa Academy of Science and Technology, Japan*; Y. Kameshima, A. Nakajima,* Tokyo Institute of Technology, Japan

We prepared ultrasmooth hydrophobic surfaces with alkyl and fluoroalkyl trimethoxysilanes, by optimizing conditions such as solvent, concentration, and reaction time. The treatment procedure was as follows; a cleaned Si wafer was immersed into a trimethoxysilane solution at room temperature. After a while, the wafer was washed with CH@sub 2@Cl@sub 2@, acetone, and water, respectively, and dried at 80°C. Water contact angle (WCA), surface roughness, and dynamic hydrophobicity (sliding angle and sliding motion of water droplet) of the prepared surfaces were evaluated. For the ultrasmooth treatment with fluoroalkyl trimethoxysilanes, it was effective to use a solution of low concentration in 1,3-bis(trifluoromethyl)benzene. With alkyl trimethoxysilanes, xylene saturated with water was better as a solvent. WCA and surface roughness increased depending on the reaction time, and sliding acceleration showed the maximal value at smallest roughness. Roughness enhanced resistance forces against sliding of a droplet. On the smooth surfaces of various silanes, a water droplet slid down with constant acceleration depending on WCA. It was found that the optimized conditions gave excellent static and dynamic hydrophobicity to Si wafer surface and that the dynamic hydrophobicity was strongly affected by the surface roughness of only a few nm. It is noteworthy that the sliding angle was significantly affected by small roughness even of the order of nm and that the sliding angles on the

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prepared smooth surfaces were almost constant, regardless of chain length and whether alkyl or fluoroalkyl.

**SS-TuP19 The Effect of Chemical Bonding on Energy Dissipation in Functionalized Silicon Resonators**, *A.M. Richter, D. Sengupta, M.A. Hines,* Cornell University

Low cost chemical or biological sensors could potentially be fabricated from micromechanical resonators, such as simple cantilevers; however, the realization of this goal has been impeded by the low performance and stability of current micromechanical devices. The sensitivity of a resonant detector is determined, in part, by its rate of mechanical energy dissipation. High mechanical energy dissipation (i.e. low quality factor, Q) leads to poor sensitivity. In previous research, we have shown that the rate of mechanical energy dissipation in MHz-range silicon resonators is profoundly affected by the chemical state of the surface. By changing a single monolayer of molecules on the surface of a 5-μm-wide, 250-nm-thick silicon resonator - less than 0.07% of the total mass - the quality factor of the resonator can be improved at least 70%. In this study, we probe the chemical origins of this effect by comparing the performance of two different types of alkyl-terminated resonators. In the first type, the alkyl chain is directly bonded to the silicon surface through a Si-C bond, whereas in the second type, the alkyl chain is bonded through a Si-O-C linkage. These monolayers were formed by the direct reaction of primary alkenes (Si-C linkage) or primary alcohols or aldehydes (Si-O-C linkage) with H-terminated silicon surfaces. The monolayers were characterized using surface infrared spectroscopy, then their affect on resonator performance was characterized using interferometric detection. Both the chemical linkage (Si-C vs. Si-O-C) and the monolayer precursor (alcohol vs. aldehyde) significantly affected performance. The chemical basis of these differences will be discussed.

**SS-TuP20 Selective Modification of Silicon-based Substrates: Reactions of Nitro-, Nitroso-, and Azido-aryls on Clean and H-terminated Si(100) and on a Surface of Silicon-filled Nanopits**, *T.R. Leftwich, S.P. Sullivan, T. Beebe, A.V. Teplyakov,* University of Delaware

The modification of silicon-based substrates has been investigated with the purpose of selective delivery of organic functional groups over a wide range of conditions. Nitro-, nitroso-, and azido-derivatives of aromatic hydrocarbons have been investigated on clean Si(100)-2x1 surface under ultra-high vacuum conditions and on H-terminated Si(100) surface under ambient conditions. These reactions were compared to analogous processes on patterned silicon-filled nanopits of 50-100 nm diameters created on a surface of highly oriented pyrolytic graphite (HOPG). The pits were created from defects formed by controlled Cs or Ga ion bombardment that were then oxidized at 923 K. These reactions were investigated using a combination of temperature-programmed desorption (TPD), infrared spectroscopy, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). While 1,3-dipolar cycloaddition dominates the attachment chemistry on a clean Si(100)-2x1 surface, reactions of H-terminated silicon with nitro-or nitroso-compounds proceed through condensation reactions, releasing a water molecule. For reactions of azido-compounds with a clean Si(100)-2x1 surface, a novel intermediate is suggested computationally and identified spectroscopically. This intermediate can be described as a nitrogen molecule stabilized on a silicon surface dimer by a neighboring aryl group. Selected surface intermediates and reaction pathways have been investigated computationally. These findings were applied to modify silicon nanostructures formed on a surface of HOPG.

**SS-TuP21 Initial Stages of the Diffusion Barrier Formation on Semiconductors: Mechanism of Decomposition of Tetrakis-(dimethylamino)-titanium on Clean and Ammonia-modified Si(100) Surfaces**, *J.C.F. Rodriguez-Reyes, A.V. Teplyakov,* University of Delaware

Tetrakis-(dimethylamino)-titanium (TDMAT) is a deposition precursor for titanium nitride and titanium carbonitride diffusion barriers. In spite of its crucial impact for the interface formation, the reaction of TDMAT with the practically important Si(100) surface has not been understood. In this work, the mechanism of decomposition of TDMAT on clean and ammonia-pretreated Si(100) surface is investigated by a combination of X-ray photoelectron spectroscopy (XPS), thermal desorption, infrared spectroscopy, and density functional theory (DFT). Adsorption of TDMAT on a clean Si(100) substrate proceeds through weak dative bonding of its ligands. Decomposition of TDMAT on a clean Si(100) surface leads to the evolution of a complex mixture of products including methane, dimethylamine and hydrogen cyanide. A chemometric approach is used to identify and quantify these compounds. The decomposition processes are analyzed on a clean Si(100) surface and compared to the ammonia-modified surface. Specific surface reactive sites produced by ammonia adsorption and thermal decomposition on Si(100) substrate have been investigated computationally and identified spectroscopically. Several previously predicted structures existing on this surface at high temperature were confirmed experimentally and a novel surface structure relevant for nitrogen diffusion was proposed. Decomposition of TDMAT on ammonia-modified surfaces is experimentally observed to be more effective than on clean Si, which provides a way to change the surface energetics by pre-treating the surface. This approach is also applied to investigating the decomposition of TDMAT on a carbon-modified Si(100) surface.

**SS-TuP22 Characterization of Orientation-Selective-Epitaxially Grown CeO$_2$ Layers on Si(100) Substrates by X-Ray Diffraction and Cross-Sectional Transmission Electron Microscopy**, *T. Inoue, S. Shida,* Iwaki Meisei University, Japan*; K. Kato,* Fukushima Technology Centre, Japan

Orientation-selective-epitaxial (OSE) growth of CeO$_2$(100) and CeO$_2$(110) layers on Si(100) substrates is found to be capable by controlling substrate bias and plasma power in reactive dc magnetron sputtering. Although we have obtained a rough growth condition map to select growth orientation,[1] at present, the detailed mechanism of OSE is not yet fully understood. In order to get insight into the origin of OSE, we characterized OSE grown CeO$_2$ layers using XRD and XTEM. The OSE growth procedure utilizing a two step growth method has been reported.[2] Firstly, we carried out XRD measurements to study the orientation components of the epitaxial layers as a function of substrate bias. Analyses of (200) and (220) peak intensity variations with substrate bias proved that (100)-oriented growth regions exist at around ±15 V bias with a half width of 5 V. In the other regions, (110)-oriented CeO$_2$ layers grow. In the vicinity of the border of the two orientation regions, XRD data contained both peaks and their intensity ratio reversed across the border. Secondly, we made XTEM observations. Lattice images of CeO$_2$(100)/Si(100) structure indicated following two facts. One is that lattice rows of CeO$_2$(100) inclined compared with those of Si(100), wherein defects such as dislocations were scarcely seen. The other is that no interfacial amorphous layers are seen when the Ce-silicide layer thickness is adequate, which indicates the advantage of the two step growth method. This is very exciting, since amorphous interfacial suboxide layers have been thought to be inevitable. A part of this work was conducted in AIST Nano-Processing Facility, supported by "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. @FootnoteText@ @footnote 1@ T. Inoue et al., J. Cryst. Growth, 271, 176 (2004).@footnote 2@ T. Inoue et al., J. Vac. Sci. Tehcnol. A 22(1), 46 (2004).

**SS-TuP23 Quantitative Analysis of SAM-Layers on Copper**, *C. Van der Marel, Y. Furukawa, N. Kahya, J.H.M. Snijders,* Philips Research, The Netherlands

Recently, a method has been developed for the quantitative analysis of XPS-measurements on homogeneous layer systems.[1] Starting from the apparent concentrations, measured at only one take-off angle, the method provides values for the composition and the thickness of all layers present in the system in a self-consistent way. The method works well for homogeneous layer systems (e.g. samples consisting of a Self Assembling Monolayer (SAM) on a substrate), provided that for each element or chemical state is known to which layer it belongs. Measurements at two or more different angles provide in general information about the depth-distribution of an element or a chemical state in a sample. The present calculation method has been extended to include measurements at two or three measuring angles; by doing so also the depth-distribution of the elements is obtained in a quantitative way. The method will be illustrated by experiments with various SAM-layers on copper. The Cu2p- and the Cu LMM lines were used to obtain information about the chemical state of copper. The copper surfaces were precleaned by means of ion etching in the XPS instrument and incubated with the appropriate SAM-layer without contact with the ambient air. @FootnoteText@ @footnote 1@ C. van der Marel, M. Yildirim and H. Stapert, J. Vac. Sci. Technol. A23 (2005) 1456 - 1470.

**SS-TuP24 Alkali Ion Scattering from Metal Nanoclusters**, *G.F. Liu, P. Karmakar,* University of California, Riverside*; Z. Sroubek,* Czech Academy of Sciences, Czech Republic*; J.A. Yarmoff,* University of California, Riverside

Neutralization during the scattering of low energy (0.5-5 keV) alkali ions provides a sensitive measure of the confined quantum states of nanomaterials. The neutral fraction (NF) for Na$^+$ scattering from

small Au clusters was previously shown to be surprisingly high (up to 50%), and to decrease with increasing cluster size.@footnote 1@ This indicated that scattered alkali ions couple to atomic-like states specific to the nanoclusters, and the energy of the states is a function of the cluster size. In this work, Na@super +@, Li@super +@ and K@super +@ ions are employed to probe the presence and position of the confined states of metal nanoclusters, and their dependence on cluster size is compared. Nanoclusters are formed by deposition of Au onto TiO@sub 2@(110), and self-organized clusters are produced from Au and Ag thin films by Ar@super +@ ion sputtering. The ion scattering NFs have different dependences with respect to cluster size for each alkali projectile. The microscopic mechanisms involved in charge exchange between the alkali ions and the nanoclusters will be discussed. @FootnoteText@ @footnote 1@G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004).

**SS-TuP25 First Principles Studies of the Reactivity of Pt Islets on Ru(0001)***, *M. Alcantara Ortigoza, S. Stolbov, T. Rahman,* Kansas State University

A key element of direct methanol fuel cells is a catalyst for electro-catalytic oxidation of methanol. However, during this reaction, intermediate CO adsorbed on the surface blocks the active sites and poisons the reactivity of commercial catalysts. It was recently reported that nanoclusters of Ru with sub-monolayer of Pt are much more tolerable to CO than commercial alloy catalysts.@footnote 1@ The mechanism of the reaction on this nano-catalyst is not clear. It apparently depends on the size of Pt islands whose optimum size is small (about 10 atoms). As a step towards understanding of the nature of this phenomenon, we have performed first principles studies, based on density functional theory, of the stability and reactivity of small Pt islands on Ru(0001), whose geometry represents that of the dominant facets of the Ru nanoparticles in the experiments of Brankovic et al. We have calculated energetics and geometric structures for 1-to 9-atom islands and one monolayer of Pt adsorbed on Ru(0001) using the pseudopotential method with the plane wave expansion for the wave function. We find the formation energy per atom of the islands to decrease monotonically from -5.1 eV to -6.1 eV, as the number of Pt atoms in the 2D island increases from one atom to one monolayer. The propensity of the systems to form as many interatomic bonds as possible thus overpowers the effect of stress caused by some misfit of Ru and Pd interatomic bonds. CO molecules are found to adsorb preferentially at the Pt island edges with a bond tilted towards the Ru atoms. The energetics of diffusion of CO and OH and their reaction pathways, as an intermediate step in methanol decomposition, are examined. @FootnoteText@ @footnote 1@S. R. Brankovic, J. X. Wang, and R. R. Adzic, Electrochem. Sol.-St. Lett. 4 (12) A217 (2001). *Work supported in part by DOE under grant DE-FG02-03ER15465 and DE-FG02-03ER46058.

**SS-TuP27 Adsorbate-Induced Faceting of Atomically Rough Re Surfaces**, *H. Wang, W.H. Chen, A.S.Y. Chan, T.E. Madey,* Rutgers University

We report faceting of atomically rough Re(12-31) and (11-21) surfaces induced by oxygen or ammonia using AES, LEED, STM and synchrotron-based high resolution X-ray photoemission spectroscopy (HRSXPS). Faceting is driven by thermodynamics (anisotropy of surface free energy) but is controlled by kinetics of surface diffusion. The Re(12-31) surface undergoes faceting once the oxygen coverage exceeds 0.5 monolayer (ML) and the surface is annealed at @>=@700K. The morphology of the surface depends on oxygen coverage and adsorption temperature, ranging from long sawtooth ridges to complex structures exposing some of the following five different facets: (11-21),(01-10),(10-10),(01-11) and (10-11). For Re(11-21), adsorption of oxygen at room temperature followed by annealing causes the surface to become partially faceted with (01-10) and (10-10) facets forming zigzag chains. Under oxidation conditions, i.e. dosing a large amount of oxygen at high temperatures (900-1000K), the (11-21) surface is completely covered by four facets identified as (01-10), (10-10), (01-11) and (10-11). In contrast, after exposure to ammonia at 700K, the Re(11-21) surface only shows a (1x2) reconstruction and remains planar (ammonia dissociates on Re, and only N remains on the surface at T>700K). By exposure to ammonia at 900K, the Re(11-21) surface becomes completely faceted, forming 2-sided ridge-like structures; the orientations of the ridge sides are different from any of those found in oxygen-induced faceting of Re(12-31) and Re(11-21). Our work demonstrates that it is possible to tailor the surface morphology by choosing appropriate adsorbate and annealing conditions, which in turn provides different but related model systems to study structural sensitivity in catalytic reactions as well as potential templates to grow nanostructures.

**SS-TuP28 Methane Activation on Nickel Surfaces: Mechanistic Insights from State-Resolved Reactivity Measurements**, *A.L. Utz, D.R. Killelea, V. Campbell, D.F. Del Sesto,* Tufts University

The molecular-level mechanism for methane activation on metal surfaces remains a subject of inquiry and debate. This has occurred in part because many experiments quantify the average reactivity of ensembles of reagents. The ensembles contain a distribution of molecules whose internal (vibrational and rotational) energies may vary significantly. The many energetic degrees of freedom available in this system severely hamper attempts to deconvolute ensemble averaging. This presentation describes experiments in which laser excitation prepares the methane reagents in specific vibrational and rotational states with well-defined total energy. We then quantify the reactivity of these state-selected molecules. Our ability to systematically vary the total energy of the reagents and its distribution among translational, rotational, and the stretching and bending vibrations of methane allows us to identify how energy deposited into specific reagent motions promotes reactivity. The presentation will highlight how these state-resolved results shed light on the mechanism for activation of methane and other hydrocarbons.

**SS-TuP29 Rebound Transitions in Surface Diffusion**, *G. Antczak,* University of Illinois

We have examined in detail the mechanism of surface diffusion on an atomic scale for the W(211) plane. Types of movement as well as their kinetics have been identified. The investigations are based on the distribution of displacements of single atoms on planes around 15 spaces in diameter. The distribution for any one temperature consists of at least 1200 observations. Special attention was paid to transient temperature effects during cooling and warming of the sample. At a temperature 1/10 the melting point we identified, in addition to standard single jumps in the direction, double jumps along as well as rebound jumps which occur when an atom starts in the direction but turns back and lands at the starting point. In the investigated temperature range we have not observed any triple jumps. The kinetics of all kinds of jumps were derived, and the correlation between different types of jumps was investigated. We found that double as well rebound jumps originate from single jumps. The increasing significance of non-nearest-neighbor transitions gradually diminishes the rate of single transitions, which almost reaches zero at 320 K. Rebound jumps start to be noticeable at 300K and seem to be quite frequent in diffusion over the W(211) plane. Surprisingly, their energy is lower then the activation energy for double transitions, 1.03 eV compared with 1.44 eV for double jumps. The reason for that is not completely clear, but possible factors involved will be presented. Research supported by the Department of Energy under Grant No. DEFG02-91ER45439 to the Materials Research Lab.

**SS-TuP30 Adsorption and Displacement of Cetyltrimethylammonium Bromide (CTAB) on Model Gold Surfaces**, *S. Lee, V.H. Perez-Luna,* Illinois Institute of Technology

The adsorption and displacement of the cationic surfactant, cetyltrimethylammonium bromide (CTAB) on model crystalline gold surfaces was studied. Adsorption of CTAB from aqueous media onto gold surfaces of different crystal orientations was studied by water contact angle measurements, spectroscopic ellipsometry, and FT-IR spectroscopy. Displacement of adsorbed CTAB molecules with 16-mercaptohexadecanoic acid (MHDA) from planar gold surfaces was performed using various MHDA concentrations and incubation times. The displacement reaction was also studied by water contact angle measurements, ellipsometry and FT-IR spectroscopy. The displacement of CTAB with MHDA on gold is evident in the decreased water contact angle upon formation of carboxyl terminated surfaces. FT-IR spectra also show differences indicative of the displacement reactions. Differences in adsorption and displacement behavior at various crystalline surfaces are especially relevant to adsorption and displacement reactions of surfactants and alkanethiols on anisotropic gold nanoparticles such as nanorods. These studies will yield new insights on strategies for surface modification of nanoparticles presenting different crystalline surfaces.

**SS-TuP31 Scanning Tunneling Microscopic Observation of Phospholipid Adlayer on Gold as a Model Cell Membrane**, *T. Yamada,* RIKEN, Japan*; S. Matsunaga, R. Yokomori,* The University of Tokyo, Japan*; D. Ino,* RIKEN, Japan*; M. Kawai,* The University of Tokyo, Japan

Microscopic view of cell membranes in the molecular scale has been desired concerning the domain structures, or "rafts", formed by various phospholipids, which are related to important biochemical functions caused by inclusion of proteins. Physical-chemistry-based model study is

needed to estimate the interaction between lipid molecules and to obtain information about domains formed with different kinds of phospholipids. We attempted to obtain STM images of phospholipid adlayer spread on modified gold substrates. First a Au(111) substrate modified by octanethiol was immersed in a neutral ammonium perchlorate buffer solution (50 mM, pH7.0), and the thiol adlayer was examined by STM within the solution. The thiol-covered surface was characterized by pores with diameters less than 10 nm, of which bottoms were also covered with thiol. Individual molecules within the adlattice were also discerned. Then the buffer solution was added with 1,2-dihexanoyl-sn-glycero-3-phosphocholine below the critical micellar concentration at 0.0 V vs. RHE of the Au electrode potential. Sequential STM images of a fluidic lipid adlayer spreading along the surface were obtained. The thickness of adlayer was observed to be a few angstroms. The motion of lipid monolayer was detected as deformation of holes on the monolayer. By changing the electrode potential to -0.2 V vs. RHE, the adlayer was gradually altered into solidified patches of striped patterns with a periodicity of 4 nm. By returning the potential to 0.0 V vs. RHE, the fluidic monolayer was restored. This change is considered related to polymerization of phospholipids. More times of potential cycling induced fragmentation of the solid striped patches. It was recognized that the functions of phospholipids are addressable on the viewpoint of nanometer-scale chemistry. The applicability of STM to lipid adlayer is promising. Some cross-checking spectroscopic evidences will be also presented.

**SS-TuP33 Enhanced Initial Hydrophilicity and Biological Response of Microstructured Titanium Implants by Chemical Modification**, *M. De Wild,* Institut Straumann AG Switzerland, Switzerland*; F. Rupp, L. Scheideler,* Poliklinik für Zahnaerztliche Prothetik Tuebingen Germany*; M. Wieland,* Institut Straumann AG Switzerland*; J. Geis-Gerstorfer,* Poliklinik für Zahnaerztliche Prothetik Tuebingen Germany*; G. Zhao, Z. Schwartz,* Georgia Institute of Technology*; D. Cochran,* University of Texas Health Science Center at San Antonio*; B.D. Boyan,* Georgia Institute of Technology
Surface topography and chemistry both influence initial wettability and peri-implant bone apposition of implants. Until now, sandblasted and acid etched (SLA) titanium surfaces are initially hydrophobic due to microstructure and contamination with hydrocarbons and carbonates. The purpose of this study was to investigate initial hydrophilicity and protein adsorption and examine its role in the response of osteoblasts on a new developed chemically modified implant surface called SLActiv. By chemical modification it is now possible to overcome the initial hydrophobic behavior of standard implant surfaces. The innovative clean-room production method influences protein/surface and cell/surface interactions in vitro. This study shows that surface energy controls osteoblast differentiation and local factor production. Histological and biomechanical observations of osseointegration approve the enhanced interactions between the SLActive implant surface and the tissue in the initial healing phase.

**SS-TuP36 Chemicurrent Caused by Adsorption of -C=C -Contained Molecules on Pt Surfaces at Low Temperature**, *M. Sushchikh, M.N. Lapushkin,* UC Santa Barbara*; H. Nienhaus,* University of Duisburg-Essen, Germany*; D. Auerbach,* Hitachi Global Storage Technologies*; E.W. McFarland,* UC Santa Barbara
A chemicurrent caused by directing beams of C=C -contained molecules (ethylene, propylene) at 100K on evaporated Pt films was measured using Schottky-type metal-semiconductor (MS) devices. Largest chemicurrent was observed for ethylene with overall yield 2*10 5 e/molecule. In the case of propylene the yield was 5*10 6 e/molecule. Increase in the kinetic energies of the impinging molecules (up to 0.5eV for ethylene and up to 0.45eV for propylene) using seeded beam techniques did not affect the chemicurrent overall yield. Beams of large molecules (benzene, propylene oxide, allylbenzene, styrene) did not cause observable chemicurrent.

**SS-TuP37 Adsorption Reaction of C2H5SH on Rh(100) Surface Studied by XPS and Sulfur K-edge NEXAFS**, *S. Yagi, T. Nomoto, A. Koizumi,* Nagoya University, Japan*; G. Kutluk,* Hiroshima University, Japan*; K. Soda,* Nagoya University, Japan*; E. Hashimoto, M. Taniguchi,* Hiroshima University, Japan
There are various environmental problems. One of the causes is automobile exhaust gas. Thereforean efficient automobile catalyst is needed for the exhaust gas (SOx, NOx, CxHy) purification. Sincethe purification catalyst loses its activity in a sulfur-containing molecular atmosphere, which is named "Sulfur Poisoning", the adsorbed sulfur have a great influence on the catalyst performance. It isimportant to investigate the reaction of sulfur containing molecules on the catalyst surface. Incomparison with other platinum group metals, rhodium especially have much resistance to the sulfur poisoning.@footnote 1@ In this investigation, we have studied the adsorption structure of C2H5SH on Rh(100)surface by X-ray Photoelectron Spectroscopy (XPS) and S K-edge Near Edge X-ray Absorption FineStructure (NEXAFS) methods. The Rh(100) surface was cleaned by the repeated operation (Ar+ sputtering and annealing) and thenexposed by C2H5SH at 85 K. Both XPS and NEXAFS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center(HSRC). C2H5SH coverage is submonolayer phase and estimated to be 0.15 ML. The S2p XPS results showthat the C2H5SH molecules dissociate to ethanethiolate C2H5S- and atomic sulfur. The C1s XPS results indicate that some hydrocarbons(CxHy) adsorb on Rh(100) surface. It is clear that theadsorbed C2H5SH, C2H5S- and hydrocarbons behaviors depend on substrate temperature. @FootnoteText@@footnote 1@ J.S.Hepburn et al., Energy & Fuels 2 (1988) 289.

**SS-TuP38 Measurement of Residual Water on Aluminum Surface by PMIRRAS**, *H.P. Hsueh,* NSRRC, Taiwan*; C.W. Yeh,* NTHU, Taiwan*; G.Y. Hsiung,* NSRRC, Taiwan*; J.R. Chen,* NSRRC and NTHU, Taiwan
Water always plays a vital role in the cleaning process of aluminum material used in UHV or XHV devices like the vacuum chambers used in large accelerators. Yet it is the residual water inside or on the thin alumina layer on top of the bulk aluminum material that was hated most in UHV or XHV regime since it is one of the major obstacles to achieve XHV. Phase modulated infrared reflection absorption spectroscopy (PMIRRAS) system has been setup and used in this study to explore how the residual water interacts with alumina surface layer of bulk aluminum as different cleaning method is applied. Both residual water quantity and their binding mechanism will be measured and analyzed. Cleaning methods include ozone water cleaning and traditional acid (HNO3+HF) and alkali (NaOH) cleaning etc. With this study, it will be determined which cleaning method has the most effective way to clean aluminum surface (contaminations less than a certain level) and yet generate either less residual water or easier repelled residual water by baking at lower temperature or shorter period. Some spectra have been measured and water spectrum at 3450 1/cm has been identified. Further analysis of obtained data will be carried out. More samples will be measured and the results will be discussed.

**SS-TuP39 The Interaction of Aluminum with 1,3,5-trinitro-1,3,5 Triazine**, *V.J. Bellitto,* Naval Surface Warfare Center, US
Vibrational and photoelectron spectroscopies have become useful tools for identifying adsorbed aromatics and their orientation on surfaces. The adsorption geometry of aromatics, such as benzene, pyridine, and triazine on Al has been deduced. On sp-metal surfaces such as on Al, benzene has been shown to adsorb in a flat-lying geometry. Although the bonding orientation is similar to that of transition metals, the bonding interaction is different with only a weak benzene-Al interaction. For the adsorption of pyridine at low temperatures and low coverages, the molecular plane is parallel to the surface plane. At higher coverages, the molecular plane tilts toward the surface normal and is bonded through the nitrogen lone pair. We have previously reported on the chemisorption of triazine on an Al (111) surface using X-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy. The data showed that some s-triazine molecules dissociatively chemisorb on the Al surface, while others adsorb intact and bond to the surface through a nitrogen lone pair. The data revealed the molecular plane of the intactly adsorbed triazine is tilted with respect to the substrate surface plane. In this work, X-ray photoelectron spectroscopy (XPS) is used to characterize the interaction of 1,3,5-trinitro-1,3,5 triazine (RDX) with Al. XPS is used to determine the chemical species at the RDX/Al interface. Besides its usefulness as a tool for chemical analysis, XPS is useful in examining changes to chemical states of materials. For RDX, the spectrum of the N 1s region has two easily discernable peaks assigned to the nitro group and ring structure nitrogen. Upon the initial interaction of aluminum with RDX, the N 1s spectrum reveals that the nitrogen peak associated with the nitro group is diminished compared to that of the ring structure. This is an indication of the preferential reaction of the nitro group with the aluminum, leaving the ring structure intact.

**SS-TuP40 Methanol Adsorption on Clean and O-Predosed V(100) Surfaces**, *M. Shen, F. Zaera,* University of California, Riverside
The reaction of methanol have been studied on the clean and O-covered V(100) surfaces. On the clean surfaces, adsorbed methanol follows various reaction pathways leading to the production of methane, carbon monoxide, formaldehyde, and ethylene the main carbon-containing desorbing compounds. Methane desorption takes places mainly in two temperature regimes centered at around 350 and 500 K. Predosing of

oxygen appears to significantly enhance the high-temperature methane production at the expense of the one at low temperatures. In addition, an upward shift is seen in the desorption temperatures of methane, ethylene and hydrogen in the presence of coadsorbed oxygen. Finally, the coupling mechanism for the formation of ethylene was investigated by using isotope labeling and also comparing the TPD spectra of several probing molecules. Our results indicated that -CH2O- and -CH2- are the most likely intermediates.

**SS-TuP41 Metallization of Self-Assembling Monolayers of Conjugated Molecules by Electroless Deposition of Cu**, *C.T. Nottbohm, A. Turchanin, A. Gölzhäuser,* University of Bielefeld, Germany

Metallization of self-assembling monolayers (SAMs) is of great interest for various areas of fundamental and applied research: fabrication of microelectronic and molecular electronic devices, establishing of electrical contacts to single molecules, metal pattering of supramolecular assemblies. Here we present an investigation of the Pd catalysed electroless deposition (ELD) of Cu on top of the amino-terminated cross-linked biphenylthiol SAMs. The lateral cross-linking and formation of amino groups have been achieved by irradiation of nitrobiphenylthiol SAMs with low energy electrons.@footnote 1@ The x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) data show that the cross-linked SAM acts as a barrier suppressing the catalyst-free ELD of Cu on the Au substrate. In order to deposit Cu on the cross-linked SAMs a Pd(0) catalyst was immobilized to their surface. This was realized by the chemical reduction of Pd(II) ions coordinated to the terminal amino groups. Angle resolved X-ray spectroscopy (ARXPS) verified every step of the Pd immobilization und unambiguously show that it forms an outermost layer of the cross-linked SAM. The AFM/XPS data show that Cu is then deposited in cross-linked areas at the catalytic site and hence on the surface of the SAM. @FootnoteText@ @footnote 1@ A. Gölzhäuser, W. Eck, W. Geyer, V. Stadler, Th. Weimann, P. Hinze, M. Grunze, Adv. Mater. 13, 806 (2001).

**SS-TuP42 Adsorption Behavior and Reaction Properties of NO and CO on the Ir Surfaces**, *I. Nakamura, A. Takahashi, M. Haneda, H. Hamada, T. Fujitani,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Selective catalytic reduction of NO in oxidizing atmospheres has recently received extensive attention, since it has potential as a practical measure to remove NOx emitted from diesel engines, lean-burn engines and combustors. A few studies of selective catalytic reduction of NO have been made with such reductants as H@sub 2@ and CO over the Ir-based catalysts. However, no evidence for explaining this reaction mechanism and the active site has been obtained. To clarify the role of CO for NO reduction, we studied the surface structure dependence for the reaction of NO and CO on the Ir single-crystal surfaces using surface science techniques such as XPS and IRAS. We examined the adsorption state of NO and CO on the Ir(111) and Ir(211) surfaces using IRAS. The peaks due to the adsorbed NO on hollow and atop sites were observed at 1400-1444 cm@super -1@ and 1799-1820 cm@super -1@ on Ir(111). On the other hand, the peaks due to the adsorbed NO on bridge and atop sites were observed at 1580-1590 cm@super -1@ and 1790-1810 cm@super -1@ on Ir(211), indicating that the NO adsorption was depended on the surface structure. Concerning the CO adsorption state, we observed the peak of CO adsorbed on atop site at 2060 cm@super -1@ over Ir(111) and at 2080 cm@super -1@ over Ir(211), indicating that the CO adsorption was not depended on the surface structure. We also investigated the thermal reactivity of the NO and CO adsorbed on the Ir(111) and Ir(211) surfaces. It was clearly demonstrated that the Ir step was active site for the NO dissociation. Furthermore, it was found that the NO reduction with CO on Ir surface proceeded via the direct decomposition of NO.

**SS-TuP43 Reactions of SO@sub 2@ and Between Atomic S and O@sub 2@ on the Ir(111) and Rh(111) Surfaces**, *T. Fujitani, I. Nakamura, M. Haneda, H. Hamada,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

It has been reported that Ir/SiO@sub 2@ shows marked catalytic activity for NO reduction with CO in the presence of O@sub 2@ and SO@sub 2@. However, no evidence was obtained for the role of SO@sub 2@. We examined the role of SO@sub 2@ for NO reduction with CO in the presence O@sub 2@. The reactions of SO@sub 2@ on Ir(111) and Rh(111) were investigated using XPS. On Ir(111), the peaks due to molecularly adsorbed SO@sub 2@ were observed after SO@sub 2@ exposure at 200 K. With the rise of temperature at 300 K, two S 2p peaks were observed at 165.9 and 162.4 eV. The peak at 162.4 eV was assigned to atomic S. The ratio of coverage of S 2p (165.9 eV) and O 1s (530.7 eV) was almost 3,

indicating that these peaks corresponded to the SO@sub 3@. After annealing to 400 K, the adsorbed SO@sub 3@ significantly decreased and the atomic oxygen was observed. The SO@sub 3@ and atomic oxygen were completely desorbed and the only atomic S was presented on the surface above 500 K. On Rh(111), SO@sub 2@ was molecularly adsorbed on the surface at 200 K. The adsorbed SO@sub 2@ dissociated to atomic S and oxygen above 300 K. The only atomic S was presented on both surfaces above 500 K, but the formation process of atomic S on Ir(111) was different from that on Rh(111). The reaction between atomic S and O@sub 2@ was examined on Ir(111) and Rh(111). On Ir(111), S coverage decreased with increasing O@sub 2@ exposure at 500 K, and then no atomic S was observed at 1000 s, indicating that atomic S reacted with surface oxygen and was removed from the surface in the presence of oxygen. In contrast, S coverage was almost constant on Rh(111). Thus, the reactivity of atomic S with oxygen on Ir(111) was significantly higher than that on Rh(111).

**SS-TuP44 Study of Dye Molecule Orientation and Configuration in Dye Molecule Doped Polythiophene Films**, *H. Kato, S. Takemura, Y. Watanabe, T. Nara, T Hayashi, T. Sugiyama, T. Hiramatsu, N. Nanba,* Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule such as crystal violet (CV) and brilliant green (BG) were prepared by electrochemical doping and casting injection methods. Electrochemical doping was conducted in dye dissolved acetonitrile by applying negative voltage in a triangle wave to an as-grown PT film. Casting of dye molecules was conducted by dipping a PT film in dye dissolved acetonitrile so that the dye molecules diffused into the polymer film. Vibrational states of the doped dye molecule and the polymer backbone were investigated by FTIR RAS and transmission measurements in order to examine the dopant orientation and configuration in polymer chains in the hybrid films. In the case of brilliant green doping, CH in plane modes of the PT backbone which appeared around 800 cm-1 was almost identical in both spectra of doped polymer and non-doped polymer. In the case of electrochemically doping sample, however, ring stretching modes which appeared around 1585 cm-1 was observed only in the FTIR transmission spectrum, not observed in the FTIR RAS spectrum. However, in the case of casting sample, the ring stretching mode was observed by both of FTIR RAS and transmission measurements. The similar results was obtained in the case of CV doped PT films. This result shows that CV and BG molecule planes doped in polymer are inclined to be planar to the film plane in the case of electrochemical doping under a negative voltage in triangle wave. In the case of casting sample, the dopants were supposed to be randomly oriented. The results suggest that the manipulation of the molecular orientation and configuration would be possible by the electrochemical doping method.

**SS-TuP45 XPS and FTIR Study of Electrochemical Doping of Fullerene and Copper Phthalocyanine Molecules in Conducting Polymers**, *H. Kato, S. Takemura, Y. Watanabe, A. Ishii, I. Tsuchida, Y. Akai, T. Sugiyama, T. Hiramatsu, N. Nanba, K. Iwasaki,* Kanto Gakuin University, Japan; *O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan

Conducting polymer polythiophene (PT) films incorporated with fullerene C60 and copper phthalocyanine (PcCu), which were highly functional molecule, were prepared by electrochemical doping and casting methods. Electrochemical doping of C60 was conducted by adopting different applying voltage polarity. C60 doping proceeded in C60 dissolved toluene by applying positive or negative voltage to a PT film. Electrochemical doping of PcCu was also conducted in PcCu dissolved toluene by applying negative voltage to a PT film. Charge transfer and interaction between the doped molecules and PT polymer chains, varied with the doping measures, were investigated by XPS analysis of the core-level energies and spectral profiles of the atomic components. Vibration states of the doped molecule and the polymer backbone were also investigated by FTIR RAS and FTIR transmission. In the case of C60 doped PT, regarding electrochemical doping, applied voltage polarity made quite a different C 1s core level spectral profiles. A large split peak associated with shifted peaks due to C60 and the charged states appeared in the case of positive polarity while serial ordered peaks with the same energy distance appeared due to C60 charged states in the case of negative polarity. In FTIR measurements, frequency position of F1u mode at 1400cm-1 , which was sensitive to charged states of C60 varied with applied voltage polarity. In the case of PcCu doped PT, PcCu-origin peaks on the higher energy side appeared in the C 1s spectrum associated with the signal detection of N 1s and Cu 2p. In FTIR measurements, characteristic vibrational modes to PcCu, in-plane, out-of-plane, and ring stretching modes were observed. Central metal-origin peak was also observed. New peaks at 1545 cm-1 and 1680 cm-1 indicates the possibility of the polymer- PcCu linkage.

**SS-TuP47 Nickel-rich Bimetallic Phosphide Hydrotreating Catalysts**, *A.W. Burns, M.E. Bussell,* Western Washington University

Our research group is interested in the design of novel transition metal phosphide catalysts to be used for the removal of sulfur from petroleum feedstocks. Hydrodesulfurization (HDS) is a process in which sulfur is catalytically removed from fossil fuels. This project focuses on the development and properties of nickel-rich bimetallic phosphide catalysts. Nickel phosphide ($Ni_2P$) has been found to exhibit high HDS activity as well as excellent stability under reaction conditions. By incorporating another metal such as Co or Fe, we are investigating the properties of bimetallic phases in order to optimize the nickel phosphide-based catalysts. Therefore, we have prepared a series of oxide-supported $Co_xNi_{2-x}P$ catalysts, where x varies between 0 and 1. Our results show an increase in HDS activity with increasing Ni (decreasing Co) compositions. Interestingly, for $Co_xNi_{2-x}P$ compositions where x is small but not zero, the HDS activity is higher than that of pure $Ni_2P$. As will be described, different results are observed for a series of $Fe_xNi_{2-x}P$ catalysts. X-ray diffraction (XRD) is used to confirm the identity of the crystalline phosphide phase(s) present, to determine the average crystallite size, and to observe the transition from the $Co_2P$-like phase to the $Ni_2P$-like phase. BET surface area and $O_2$ chemisorption capacity measurements are used to determine the surface area and the number of active sites for the oxide-supported catalysts. Together with the results of elemental analysis and x-ray photoelectron spectroscopy (XPS) measurements, the surface area and chemisorption data are used to describe how the HDS activity is influenced by the surface properties of these catalysts. In this manner, we are determining the optimal composition for Ni-rich bimetallic phosphide catalysts for the HDS process.

# Wednesday Morning, November 15, 2006

## Nanometer-scale Science and Technology
## Room 2016 - Session NS+SS+TF-WeM

### Nanotribology and Nanomechanics
**Moderator:** J. Harrison, U.S. Naval Academy

**8:00am NS+SS+TF-WeM1 Nanotribological Properties of Diamond-Like Carbon Thin Films: The Effect of Annealing on Nanoscale Adhesion and Friction**, *D.S. Grierson, A.R. Konicek, A.V. Sumant, K. Sridharan, R.W. Carpick,* UW-Madison

Developing micro- and nano-scale devices with contacting or sliding parts continues to be challenging due to the poor tribological performance of conventional materials at the micro/nanoscale. The surface-to-volume ratio at small scales is high, and therefore materials with low nanoscale adhesion, friction and wear are needed to reduce tribological failures. Additionally, in applications where materials are subjected to cyclic thermal loadings, such as nanoscale thermomechanical data storage, the structure and tribological properties must remain stable. Diamond-like carbon (DLC) thin films have exceptional physical, chemical and tribological properties at the macroscale and are promising candidates for tribologically robust micro/nanoscale devices. We have studied the surface chemistry and nanotribology of undoped, Si-containing, and F-containing DLC, and investigated how annealing these films at 300°C in air affects these properties. We used the XANES (x-ray absorption near-edge spectroscopy), a surface-sensitive probe of the core-hole perturbed local density of unoccupied states, to understand the evolution of the surface chemistry and bonding. The $sp^3/sp^2$ ratio is increased by the addition of Si but not by F. The Si-containing DLC shows increased thermal stability. Atomic force microscopy (AFM) with DLC-coated AFM tips was used to conduct self-mated nanotribology experiments. The AFM results indicate that all DLC films exhibit adhesion on the order of van der Waals forces ($\sim$0.03 $J/m^2$), and the nanoscale adhesion and friction on the Si-containing DLC are not affected by the thermal annealing. This indicates that DLC films, particularly those doped with Si, are highly promising for nanoscale thermomechanical device applications.

**8:20am NS+SS+TF-WeM2 Spectromicroscopy of Tribochemistry: X-PEEM Characterization of Wear vs. Humidity for Ultrahard Carbon Films**, *A.R. Konicek, D.S. Grierson, A.V. Sumant,* UW-Madison; *N.N. Naguib, O. Auciello, J.A. Carlisle,* Argonne National Lab; *T.A. Friedmann, J.P. Sullivan,* Sandia National Labs; *J. Birrell,* Advanced Diamond Tech.; *P.U.P.A. De Stasio, R.W. Carpick,* UW-Madison

The outstanding tribological performance of carbon-based films can be seriously affected by variations in humidity. To explore the tribochemical origins of this behavior, self-mated interfaces of tetrahedral amorphous carbon (ta-C) and ultrananocrystalline diamond (UNCD) films were subjected to fretting wear in dry N2 with relative humidity values of 0%, 25% and 50%. Relative friction was measured during fretting, and the resulting wear tracks were examined with atomic force microscopy (AFM) and X-PEEM-XANES (X-ray PhotoElectron Emission Microscopy combined with X-ray Absorption Near-Edge Structure) spectromicroscopy. X-PEEM is capable of discerning chemical and bonding contrast at high spatial resolution, readily distinguishing between the wear track and the unworn film. For both films, friction increases as the relative humidity decreases. However, there are opposing trends in the behavior of graphitization and oxidation due to wear. For ta-C, as the relative humidity is decreased there is an increase in both graphitization and oxidation. This implies that the harsher wear environment has more heavily modified the carbon bonds compared to the wear at a higher relative humidity, inducing graphitization and oxidation. In contrast, the self-mated UNCD interface showed a comparative decrease in graphitization and oxidation in the wear track as the relative humidity was decreased. We will discuss changes observed in both friction and the chemical signature of the surface as the amount of relative humidity in the environment is varied. We will also discuss the relation between the amount of relative humidity in the environment and the level of graphitization that occurs in the wear track. @FootnoteText@ This work was partially supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

**8:40am NS+SS+TF-WeM3 The Role of Atomic Corrugation, Crystal Orientation, and Surface Chemical Bonding in the Nanotribology of Carbon-Based Systems**, *R.W. Carpick,* University of Wisconsin-Madison **INVITED**

A key challenge for nanotechnology lies in developing an understanding of nanotribology, particularly for materials with outstanding tribo-mechanical properties such as carbon-based films. Frictional slip and wear in these materials can be manifested in unique and surprising ways. As a fundamental example, we show that nanoscale friction can exhibit clear transitions from smooth sliding to single slips and then multiple slips. The slips are directly correlated with the atomic lattice of the sample, in this case pure graphite. The observation of the transition to multiple slips is new, and is understood by considering the competition between the stiffness of the interatomic interfacial potential and the elastic stiffnesses of the contacting materials and the force sensor itself. The transition to smooth sliding with ultralow dissipation in open air is observed for the first time, and atomic-scale stick-slip is observed for interfaces orders of magnitude larger than any previously tested. Atomic-scale stick-slip may therefore be a far more prevalent phenomenon than currently appreciated. We have also extensively studied the nanotribological behavior of other carbon-based systems, including single crystal and nanocrystalline diamond. The atomic structure of the surface, verified by detailed surface spectroscopy, critically affects friction and adhesion. Hydrogen termination is particularly effective in reducing friction and adhesion to the limit of van der Waals' interactions. Friction and adhesion are also affected by the crystal orientation. For larger tips, continuum mechanics models of contact area can be applied to understand the interfacial mechanics of these nano-scale contacts, as evidenced by the observation of direct proportionality between friction and contact area, a phenomenon known as "interfacial friction". By using smaller tips coated with a carbonaceous film, the limits of continuum mechanics are explored and discussed.

**9:20am NS+SS+TF-WeM5 Influence of the Solvent Environment on the Contact Mechanics of Tip-Sample Interactions in Friction Force Microscopy of Self Assembled Monolayers**, *T.J. Colburn, G.J. Leggett,* University of Sheffield, UK

The application of friction force microscopy (FFM) to the characterisation of surface composition and nanoscale tribological phenomena requires an adequate understanding of the tip-sample contact mechanics. We present new data that show that the properties of the liquid medium influence not only the strength of the frictional interaction in FFM, but also the nature of the contact mechanics model that describes the tip-sample interaction. FFM measurements have been carried out on self assembled monolayers of dodecanethiol ($C_{10}CH3$) and mercaptoundecanoic acid ($C_{10}COOH$) in a variety of liquid media using tips functionalised with alkanethiols (chemical force microscopy). In perfluorodecalin, a liquid with a low dielectric constant, the friction-load relationship fits the behaviour predicted using the Johnson-Kendall-Roberts model for like pairs of interacting molecules, and the Derajuin-Muller-Toporov model for unlike molecules. In contrast, measurements in ethanol, a liquid with a larger dielectric constant, obey Amontons' law (i.e. the friction force is linearly proportional to the load). These findings suggest that single asperity contact mechanics are observed in media with low dielectric constants, where dispersion forces are very strong and frictional interactions are adhesion-controlled. In media with large dielectric constants, sliding is not adhesion-controlled and linear friction-load behaviour is observed.

**9:40am NS+SS+TF-WeM6 Indentation of Individual and Multiple Multi-Walled Carbon Nanotubes with AFM**, *H.W. Yap, R.W. Carpick,* University of Wisconsin-Madison

There has been a recent surge of theoretical interest in the axial compression of MWCNTs, but only a limited number of experimental studies have been conducted. The study of axial compression of MWCNTs sheds light on their mechanical properties and has interesting implications in the fabrication of CNT - based composites. Lakes et al.@footnote 1@ have shown that macroscopic tubes have better damping properties in the post kink - buckled, snap-through regime, which is marked by a force drop with increased compression. Waters et al.@footnote 2@ and Qi et al.@footnote 3@ have indented an array of vertically aligned MWCNTs but have not observed force drops indicating these snap-through instabilities. Here, a stiff AFM cantilever with a microsphere tip attached to it is used to indent and compress a film of vertically-aligned MWCNTs with aspect ratio of ~35. These CNTs are grown with dc plasma-enhanced hot filament chemical vapor deposition from an anodized alumina nanopore template.

This is the first use of spherical probe AFM to compress aligned CNTs, though this method has been widely used in indenting biological and polymeric materials. Continuous cycles of loading and unloading to large strains were performed, and both large drops and finer relaxations in the loading portions of the force curves of a collection of MWCNTs were observed with a high degree of reproducibility. The drops are likely signatures of collective kink buckling instabilities seen in individual CNTs. The deformations, while nonlinear, are mostly elastic and reversible, as demonstrated by SEM images of the spherical tip and the sample after many cycles of deformation. We will discuss the implications of these results in the design of composites that take advantage of buckling instabilities for high damping applications. @FootnoteText@ @footnote1@Lakes et al.,Phil.Mag.Lett.,81,95(2001). @footnote2@Waters et al.,Appl.Phys.Lett.,85,1787(2004) @footnote3@Qi et al.,J.Phys.Mech.Sol.,51,2213(2003).

**10:40am NS+SS+TF-WeM9 Measurements and Modeling of Shear Modulus of Multiwalled Tungsten Disulfide Nanotubes**, *I. Kaplan-Ashiri, S.R. Cohen, N. Apter, H.D. Wagner, R. Tenne,* Weizmann Institute of Science, Israel*; G. Seifert,* Technische Universitat Dresden, Germany*; R. Shneck, D. Barlam,* Ben Gurion University, Israel

Recent investigations of the mechanical properties of inorganic fullerene have highlighted their unique properties.@footnote 1@ Although the bending modulus has been measured on single nanotubes, the shear modulus is much smaller and technically more difficult to ascertain. The S-W-S sandwich structure of individual layers of these inorganic nanotubes distinguish them chemically and mechanically from carbon nanotubes. The spacing of 6.18Å between layers is comprised of the tungsten disulfide entity, and a van der Waals gap. Direct measurements of the shear modulus of single tubes could elucidate how the tube mechanics are influenced both by the gap, and the interaction between the adjacent dichalcogenide atomic layers. Measurements were made in a scanning probe microscope (SPM) using a method similar to that described by Wu et al.:@footnote 2@ Nanotubes were dispersed on a grid structure consisting of trenches of depth 200 nm and width 500 nm. Scanning electron microscopy (SEM) was used to locate nanotubes which were appropriately aligned, and suspended over such a trench. These nanotubes were then glued to the substrate at the trench edge with amorphous carbon.@footnote 3@ The SPM was subsequently used to bend the suspended nanotubes from the side with the SPM probe by amounts ranging between 5 and 100 nm, while recording the lateral force. The results were analyzed by applying the bending equation using the known value of the bending modulus to extract shear modes. Results were further compared with both density functional calculations, and finite element analysis modeling, providing insights into mechanical interactions between the layers. @FootnoteText@ @footnote 1@ I. Kaplan-Ashiri, et al, Proc. Nat. Acad. Sci. 103, 523 (2006).@footnote 2@ B. Wu, et al, Nature Mat. 4, 525 (2005).@footnote 3@ Yu et al, Science 287, 147 (2000).

**11:00am NS+SS+TF-WeM10 Deformation Behavior of Low-Density Nanoporous Dielectrics***, S.O. Kucheyev, P.M. Bythrow, T.F. Baumann, C.A. Cox, Y.M. Wang, T. van Buuren, A.V. Hamza,* Lawrence Livermore National Laboratory*; J.E. Bradby,* The Australian National University

Understanding deformation behavior of nanoporous glasses has recently regained tremendous interest in the community, primarily due to its importance for the development of a new generation of low-k dielectrics. Aerogels are sol-gel-derived nanoporous dielectric materials formed by nanometer size particles randomly interconnected into a solid network with a large degree of porosity and very high surface area. For these materials, the density can be varied from the theoretical maximum density (of a full density solid) to extreme cases of very high porosities (~99 %). Thus, aerogels represent a very attractive model system for studying the deformation mechanisms in nanoporous dielectrics. In this presentation, we discuss the use a combination of sound velocity measurements and nanoindentation with large spherical indenters (1-2 mm diameter) to study the deformation behavior of alumina and tantala aerogels with porosities up to 99%. In particular, we focus on how the deformation behavior is affected by (i) the average density of monoliths, (ii) the morphology and connectivity of nanoligaments, and (iii) the crystallographic phase. Results show that all of the above parameters can strongly affect the mechanical properties of nanoporous solids. Based on our results, we discuss the underlying deformation mechanisms and demonstrate an effective way to control mechanical properties of the nanoporous solids that can be synthesized with ligaments having a quasi-two-dimensional shape, such as platelets, ribbons, or leaflets. Work at LLNL was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

**11:20am NS+SS+TF-WeM11 Nanoporous Au - a 3D Network of Ultra-High Strength Nanowires***, J. Biener, A.M. Hodge, J.R. Hayes, M. Duchaineau, L.A. Zepeda-Ruiz, A.V. Hamza, F. Abraham,* Lawrence Livermore National Laboratory

Recent mechanical studies on nanoporous gold (np-Au) have revealed that the yield strength of this material is almost one order of magnitude higher than predicted by scaling equations developed for open-cell foams. The higher-than-expected yield strength seems to be linked to the nanoscale morphology of np-Au which can be best described as a three-dimensional network of ultra-high strength Au nanowires. Here, we compare experimental results with molecular dynamics simulations to elucidate the nature of the high yield strength of nanoporous gold. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48.

**11:40am NS+SS+TF-WeM12 Superconductivity Dependent Friction of Water, Nitrogen and Superheated He Films Adsorbed on Pb(111)***, J. Krim, M. Highland,* North Carolina State University

The ability to predict sliding friction in adsorbed film systems underlies a vast range of topics in physics and nanotechnology, spanning the origins of static friction to the design of atomic-scale automobiles. One still hotly debated topic in this area is the degree to which electronic effects contribute to friction. In order to explore this issue, we have performed a quartz crystal microbalance study of sliding friction levels in nitrogen, water and superheated helium films adsorbed on Pb(111)@footnote 1@ and also self-affine fractal Pb substrates alternating in and out of the superconducting state. Reductions in friction upon entry into the superconducting state are greater for nitrogen than helium, consistent with a recent theory that linked electronic friction to adsorbate polarizability. Repetitive cycling of the externally applied magnetic field is observed to reduce overall friction levels.@footnote 2@ @FootnoteText@ @footnote 1@ M. Highland and J. Krim, Phys. Rev. Lett., in press (2006)@footnote 2@ Work supported by NSF and AFOSR.

**12:00pm NS+SS+TF-WeM13 In Situ Quantitative TEM Nanoindentation of Individual Nanoparticles and Nanoscale Materials***, Z. Shan, A.M. Minor,* Lawrence Berkeley National Laboratory*; S.A. Syed Asif, O.L. Warren,* Hysitron Inc.

Monitoring the microstructure evolution while simultaneously measuring the stress and strain information at the nanometer level has been a long standing goal for material scientists. Here we show that by incorporating a miniature capacitive transducer into a TEM holder the load-displacement response (force resolution better than 0.5 ÂµN and displacement resolution better than 1 nm) can be achieved inside a TEM during the in situ nanoindentation process. A wide range of materials have been examined using this technique, such as Al thin films, single crystal Ni and Cu, Au and Cd metallic nanoparticles, and hollow shell-structured nanoparticles. The preliminary results will be reported and the physical insight derived from these results will be discussed. In particular, our results demonstrate unique insight into the initial deformation processes during the nanoindentation of metals and the analysis of elastic moduli and plasticity in nanoparticles.

## Surface Science
## Room 2002 - Session SS1-WeM

### Reactions on Metal & Bimetallic Surfaces
**Moderator:** B.E. Koel, Lehigh University

**8:00am SS1-WeM1 Modes of Alloy Crystal Growth Dominated by Sub-Surface Defect Dynamics***, J.P. Pierce, N.C. Bartelt, K.F. McCarty,* Sandia National Laboratories                                                    **INVITED**

We show that the evolution of an alloy's surface during film deposition can be controlled by phenomena typically thought of as bulk or sub-surface processes. The response of a two-element compound, NiAl, is observed in real time with low-energy electron microscopy as one element, Al, is deposited on its surface. At low temperature (<600 K), this is a conventional heteroepitaxial system; the NiAl is a template on which increasingly Al-rich film phases grow. At higher temperatures, however, the substrate actively participates in the crystal growth by supplying a flux of Ni atoms to the surface. New layers of NiAl alloy form on the substrate even

though only Al is deposited. As more Al is deposited, initially immobile bulk dislocations dissociate and move, and new atomic layers nucleate along their tracks. This behavior is unlike typical epitaxial growth in two ways. First, the compositions of the deposited and growing materials differ - Al is deposited but NiAl grows. Second, localized changes in the surface's topography and composition accompany the dislocation motion. These dynamics relate simply to the type and abundance of point defects in the near-surface region. Quantitative analysis shows that exactly half of the deposited Al atoms replace Ni in the bulk and the other half incorporate into new NiAl on the surface, establishing that Ni antisites are the point defects that initially supply Ni to the surface for NiAl growth. Analysis also shows that dislocations begin to move when the near-surface concentration of these defects is depleted to the critical composition below which Ni vacancies form. We find that the crystallographic direction of dislocation motion changes with composition. Finally, we describe how the motion of dissociated (partial) dislocations both locally enhances the crystal growth rate and changes the local composition. This work supported by U. S. DOE, OBES, Division of Materials Sciences under contract DE-AC04-94AL8500.

**8:40am SS1-WeM3 CO Adsorption on a Transition Metal Quantum Well System: fcc Co/Cu(100)\***, *L. Tskipuri, H. Yao, 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. The 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 the strength of CO boding to Cu MQW overlayers on the pseudomorphic fcc-Co/Cu(100) and fcc-Fe/Cu(100) systems. Here we 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 fccCo/Cu(100) system using inverse photoemission (IPE) and temperature programmed desorption (TPD), respectively. As-grown Co films exhibit well-defined MQW states that disperse upward with increasing film thickness, but are less pronounce than on other similar systems owing to partial overlap of exchange spit states. Upon CO adsorption a well-defined structure centered about 3.8 eV above the Fermi level appears and is assigned to the unoccupied CO $2\pi^*$ 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 (~ 120K), 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. We have observed similar desorption peak temperature shifts when CO desorption from the Ni/Cu(100) system is compared to single crystal Ni(100). The CO desorption temperature varies with Co layer thickness and the possible role of quantum size effects on the molecule-surface bond will be discussed. @FootnoteText@ * funded by the Petroleum Research Fund.

**9:00am SS1-WeM4 Interaction of O@sub 2@, CO, and Methanol with Bimetallic Model Catalysts**, *T. Nowitzki, B. Juergens, H. Borchert,* University of Bremen, Germany; *S. Giorgio,* CRMCN-CNRS, France; *T. Risse,* Fritz-Haber-Institut, Germany; *V. Zielasek,* University of Bremen, Germany; *C. Henry,* CRMCN-CNRS, France; *H.-J. Freund,* Fritz-Haber-Institut, Germany; *M. Baeumer,* University of Bremen, Germany

Bimetallic particles may exhibit catalytic activities which reach far beyond those of the monometallic components. For the Co/Pd combination which is, e.g., of technological relevance for the hydrogenation of CO on the route from natural gas to liquid fuel, we have studied the interaction with CO, O@sub 2@ and methanol on the molecular scale. As a model system, mono- and bimetallic nanoparticles were prepared under UHV conditions by physical vapour deposition on a thin alumina film grown on a NiAl(110) single crystal. Bimetallic particles were obtained by sequential deposition of the two metals. The composition of these particles depends on the succession of metal depositions: depositing Co first leads to Co-core Pd-shell particles, whereas depositing Pd first results in separated Pd crystallites with a Co shell and Co nanoparticles in between. Upon O@sub 2@ deposition at room temperature, monometallic Co clusters completely oxidize as revealed by XPS and TPD. Yet, the particles can be reduced by heating to temperatures above 550K. While XPS indicates mostly metallic Co, both, metallic and oxidic components are detected in TPD, pointing to a thin persistent surface oxide layer. Upon CO deposition on metallic Co

particles we find significant CO dissociation above room temperature, which may be relevant for the CO hydrogenation. Methanol, which is known to dissociate at Pd nanoparticles, was exposed to monometallic Co and bimetallic Co-Pd particles to determine if and how the composition of the particles influences methanol decomposition and oxidation. In order to relate the investigation of the UHV model systems to technologically relevant catalytic processes, we have performed turn-over experiments for CO oxidation and methanol decomposition in ambient conditions at bimetallic particles of well-defined atomic structure. Surface adsorbate species were analyzed by IR spectroscopy.

**9:20am SS1-WeM5 Bimetallics - From Theory to Catalysis of Olefin Oxidation**, *M.A. Barteau,* University of Delaware  **INVITED**

The overall strategy of our research is to utilize first principles approaches: Density Functional Theory (DFT) calculations and surface science experiments, to understand surface reaction mechanisms and to design new and improved heterogeneous catalysts. This has led to the demonstration of new bimetallic catalysts for the oxidation of ethylene to ethylene oxide. The key has been the demonstration, utilizing experimental and theoretical tools in concert, of surface oxametallacycle intermediates as the species that control the selectivity of this reaction. This discovery permits the influence of catalyst promoters on selectivity to be probed, and new catalyst formulations to be developed. We have proposed a new mechanism of catalyst promotion for this system by alkalis based on surface ion-dipole interactions. We have predicted, using DFT, that Cu-Ag bimetallic catalysts should offer improved performance over silver alone, and have confirmed this prediction by experiment. This represents one of the first examples of catalyst design for improved selectivity based on first principles approaches.

**10:40am SS1-WeM9 'Live' Observations of Working Catalysts with STM and X-rays at High Pressures**, *J.W.M. Frenken,* Leiden University, The Netherlands, Netherlands; *B.L.M. Hendriksen,* Lawrence Berkeley National Laboratory; *S.C. Bobaru, M.D. Ackermann,* Leiden University, The Netherlands  **INVITED**

We employ scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) to obtain direct information on the structure and the atomic and molecular processes that occur on the surface of a catalyst while it is active in a chemical reaction under the high-temperatures and high-pressures conditions typical in catalysis. STM-movies obtained during the oxidation of CO on Pt and Pd surfaces, demonstrate that at high O@sub 2@ pressures the surface oxidizes and the reaction changes from a Langmuir-Hinshelwood to a Mars-Van-Krevelen mechanism.@footnote 1,2@ We resolve various ultrathin oxide structures, which only appear under high partial pressures of oxygen.@footnote 3@ Finally, we introduce a new explanation for self-sustained oscillations in the reaction rate@footnote 2@, which involves a novel role for atomic steps in catalysis.@footnote 4@ @FootnoteText@ @footnote 1@ B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev.Lett. 89, 046101 (2002).@footnote 2@ B.L.M. Hendriksen et al., Surf.Sci. 552, 229 (2004).@footnote 3@ M.D. Ackermann et al., Phys.Rev.Lett. 95, 255505 (2005).@footnote 4@ B.L.M. Hendriksen et al., to be published. .

**11:20am SS1-WeM11 Pinpointing where CO Molecules Reside and React on Stepped Surfaces**, *J.N. Andersen, A. Resta, E. Lundgren, A. Mikkelsen,* Lund University, Sweden

The geometrical as well as the electronic structure in the vicinity of steps differs from that on the flat parts of the surface. These differences often significantly influence the adsorption of and reactions amongst adsorbate molecules and atoms. As small particles used for instance in catalysis has a high concentration of steps, step induced reactions may be dominant for such particles. In the present contribution we demonstrate that the C1s binding energy as measured by high resolution core level spectroscopy (HRCLS) can be used to pinpoint if CO molecules are adsorbed at steps on a number of vicinal surfaces and discuss why this is so. We give a number of examples of how this can be utilized for obtaining information related to the CO adsorption and to oxidation reactions of the CO molecules. We demonstrate how HRCLS measurements on a Pt(332) surface in thermodynamic equilibrium with an in-situ CO background pressure directly demonstrate a higher CO adsorption energy at the steps. Measurements from different vicinal Rh surfaces show that the specific facet present at the steps has a significant influence on the adsorption sites taken by CO molecules on the terraces at higher CO coverage. Finally, we show that this methodology allows pinpointing that oxidation of CO on a vicinal Pt(332) surface proceeds via the reaction with a 1D oxide exclusively found at the steps.

**11:40am SS1-WeM12 Adsorption of Gas-Phase Oxygen Atoms on Pt(100)-hex-R0.7°**, *R.B. Shumbera, H.H. Kan, J.F. Weaver,* University of Florida
We investigated the adsorption of gaseous oxygen atoms on Pt(100)-hex-R0.7° at surface temperatures of 450 and 573 K using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (ELS), and low energy electron diffraction (LEED). Differences in the O@sub2@ TPD spectra reveal that the types and relative populations of the oxygen phases that develop on Pt(100) are strongly dependent on the surface temperature during adsorption. At 573 K, oxygen atoms initially adsorb into disordered (3x1) domains up to a coverage of about 0.32 ML (monolayers), and then arrange into a complex, ordered phase until the surface saturates at a coverage of 0.63 ML. In contrast, chemisorption at 450 K results in the simultaneous growth of the disordered (3x1) phase as well as a "high-concentration" phase that populates at the expense of the complex, ordered phase up to a coverage of about 0.50 ML. The temperature dependence of the oxygen phase distribution suggests that slow kinetics hinders formation of the complex, ordered phase, and forces oxygen atoms to become trapped in the high-concentration phase at 450 K. Further atomic oxygen uptake at 450 K produces an additional disordered phase that acts as a precursor to the growth of three-dimensional Pt oxide particles that saturate at approximately 3.6 ML for the incident fluxes employed. Finally, thermal decomposition of the Pt oxide is characterized by an explosive O@sub2@ desorption peak that shifts to higher temperature and intensifies dramatically as the initial oxygen coverage is increased, similar to prior observations on Pt(111).

**12:00pm SS1-WeM13 Fluctuation Effects in Nanoscale Surface Reaction Systems: Influence of Reactant Phase Separation during CO Oxidation**, *D.-J. Liu, J.W. Evans,* Ames Laboratory (USDOE)
For catalytic surface reactions on supported metal nanoclusters@footnote 1@ or on the nanofacets of metal field-emitter tips,@footnote 2@ strong fluctuation effects can significantly impact behavior. A realistic atomistic multi-site lattice-gas model@footnote 3@ is used to assess such behavior in nanoscale CO-oxidation systems at lower temperatures (or higher pressures). Here, adspecies interactions and the availablity of various adsorption sites play an important role due to higher reactant adlayer coverages. Time-series for coverages and related quantities reveal fluctuation-induced transitions between distinct states associated with phase separation of reactant adspecies (in addition to transitions between stable reactive and inactive states associated with the Langmuir-Hinshelwood reaction mechanism). The former are plausibly observed in field-emission-microscopy studies.@footnote 2@ We also characterize unusual features of hysteresis analyses in this regime, and assess the role played by defects in enhancing transitions. @FootnoteText@ @footnote 1@ V. Johanek et al., Science 304 (2004) 1639.@footnote 2@ Y. Suchorski et al., Phys. Rev. Lett. 82 (1999) 1907.@footnote 3@ D.-J. Liu and J.W. Evans, J. Chem. Phys. 124 (2006) 154705.

## Surface Science
## Room 2004 - Session SS2-WeM

### Electronic and Vibrational Excitations and Dynamics
**Moderator:** M. Trenary, University of Illinois, Chicago

**8:00am SS2-WeM1 Theory of Electron-Hole Pair Excitation in Chemisorption**, *M.S. Mizielinski, D.M. Bird,* University of Bath, UK*; M. Persson, S. Holloway,* University of Liverpool, UK
It has long been recognised that the excitation of electron-hole pairs is an important mechanism for the transfer of energy to a surface in the adsorption of molecules on metal surfaces. Interest in electron-hole pair excitation has been revived recently with the observation of 'chemicurrents'@footnote 1@ and exo-electron emission following vibrational de-excitation.@footnote 2@ These phenomena are fundamentally non-adiabatic processes and require a theoretical description which goes beyond the Born-Oppenheimer approximation. To do this using ab-initio time-dependent DFT is computationally very expensive. Our approach is to gain an insight into the adsorbate-surface interaction by considering a simple model system. We analyse the non-adiabaticity by solving the time-dependent, mean-field Newns-Anderson model in the wide-band limit. In our previous work@footnote 3@ we have used this model to explore the non-adiabatic behaviour of the occupation of the adsorbate energy levels and the energy transfer between adsorbate and the metal surface. We present an extension of this work to an analytic solution for the time-evolving spectrum of excited electrons and holes. We

will use this model to demonstrate the evolution of the excitation spectrum for a range of model systems. @FootnoteText@ @footnote 1@ B. Gergen et al., Science 294, 2521 (2001).@footnote 2@ J. D. White et al. Nature 433, 503 (2005).@footnote 3@ M. S. Mizielinski, D. M. Bird, M. Persson and S. Holloway, J. Chem. Phys. 122, 084710 (2005).

**8:20am SS2-WeM2 Adsorption-State-Dependent Subpicosecond Photoinduced Desorption Dynamics**, *P. Szymanski, A.L. Harris,* Brookhaven National Laboratory*; M.G. White,* Brookhaven National Laboratory and SUNY Stony Brook*; N. Camillone III,* Brookhaven National Laboratory, Suffolk
Femtosecond laser excitation has been used to initiate desorption of molecular oxygen from the (111) surface of Pd and study the adsorption-state-dependence of the substrate-adsorbate coupling. The relative populations of the two chemical states, peroxo (O@sub 2@@super 2-@) and superoxo (O@sub 2@@super -@), were varied by changing the total coverage. Two-pulse correlation measurements reveal that the O@sub 2@-substrate coupling times are dominated by a sub-500 fs response that is independent of O@sub 2@ coverage. In contrast, the measurements show a systematic coverage dependence of the photodesorption yield and the nonlinearity of the fluence-dependence. Thus, though the photoinduced desorption from the two states is driven primarily by the same electron-mediated mechanism, the desorption efficiency from the superoxo state is greater than that from the peroxo state. These results are discussed in the context of the two-temperature model, treating the dependence of the desorption yield on absorbed laser fluence together with the dynamics in a global simulation to extract coupling strengths and understand the adsorption-state-dependence of the desorption efficiency.

**8:40am SS2-WeM3 High Resolution Photoemission as a Probe of the Collective Excitations in Condensed Matter Systems**, *P.D. Johnson,* Brookhaven National Laboratory **INVITED**
Recent advances in photoemission are allowing detailed studies of the role of collective many-body excitations in the decay of a photohole. The collective excitations include phonons, charge density waves and magnetic or spin excitations. With these developments angle resolved photoemission with its momentum resolving capabilities has become a powerful probe of the transport properties in condensed matter systems. We review these advances and examine the application of photoemission to studies of both metallic systems and strongly-correlated materials. The latter exhibit a rich variety of phenomena including high Tc superconductivity. In particular, we examine the nature of the low-energy excitations and the role of dimensionality.

**9:20am SS2-WeM5 The Origin of Work function Changes Induced by Adsorbates on Metal Surfaces: A Theoretical Analysis**, *P.S. Bagus,* University of North Texas*; C. Wöll,* Ruhr-Universität Bochum, Germany
Adsorbates may induce large shifts in the work function, @phi@, of a metal surface. A traditional explanation of work function changes has been in terms of charge transfer, CT, between the substrate and the adsorbate with CT from the adsorbate to the substrate leading to a decrease in @phi@ and to an increase in the interface dipole, as for alkali atom adsorbates.@footnote 1@ For covalently bonded CO/Cu, the CT interpretation of @DELTA@@phi@>0 suggests a Cu-CO interaction dominated by @sigma@ donation.@footnote 2@ However, weakly bound physisorbed adsorbates@footnote 3@ on metal surfaces also induce large @DELTA@@phi@ and this cannot easily be explained by CT. For physisorbed species, the Pauli exclusion principle, which requires that an electronic wavefunction is anti-symmetric, has been shown@footnote 3,4@ to make a large contribution to the @DELTA@@phi@. On Cu(111), we have studied the @DELTA@@phi@ induced by several adsorbates, Xe, C@sub 6@H@sub 12@, C@sub 6@H@sub 6@, CO, Cs, and I, representative of quite different types of bonding to the surface. The origins of the changes in the interface dipole are interpreted based on a decomposition into individual contributions from: (1) Pauli exclusion; (2) Polarization of the metal substrate; (3) Covalent bonding; and (4) Charge transfer. More than one contribution to @DELTA@@phi@ may be large. The theoretical approach used is based on ab initio electronic structure theory applied to models of an adsorbate on a cluster of atoms representing the surface.@footnote 4@ We provide a unified understanding that makes it possible to correctly relate @DELTA@@phi@ to the chemistry of the adsorbate-substrate bond. @FootnoteText@ @footnote 1@J. P. Muscat and I. P. Batra, Phys. Rev. B, 34, 2889 (1986).@footnote 2@D. Heskett et al., Phys. Rev. B, 32, 6222 (1985).@footnote 3@P. S. Bagus, V. Staemmler, and C. Wöll, Phys. Rev.

Lett., 89, 096104 (2002).@footnote 4@P. S. Bagus, K. Hermann, and C. Wöll, J. Chem. Phys. 123, 184109 (2005).

**9:40am SS2-WeM6 Rotational Disorder in Ordered Overlayer Phases**, *E.Z. Ciftlikli, I.G. Shuttleworth, A.V. Ermakov, J. Lallo, S. Rangan,* Rutgers, State University of New Jersey; *S.D. Senanayake,* Oak Ridge National Laboratory; *B.J. Hinch,* Rutgers, State University of New Jersey

CN containing moieties, such as C@sub 2@N@sub 2@, CN@super -@, CH@sub 3@CN and NCO species, are frequently observed as reactants, products and intermediates in many industrial heterogeneous catalytic processes. Despite their importance, there are relatively few published reports on the structure and dynamics of these species on metallic fcc close packed faces. It may be that electron and/or photon induced damage has hindered many such studies. Helium atom scattering (HAS), employing thermal energy atoms of E<100 meV, is free of any detrimental/destructive effects. For example, angle resolved HAS measurements clearly show the existence of c(10x6) and c(2x2) ordered structures for CN@super -@/Cu(001) and CH@sub 3@CN/Cu(001) surfaces, respectively. And yet energy resolved HAS measurements, which are designed to probe the low-energy vibrational modes of the bound moieties, do not indicate discrete low energy features associated with of localized modes of the adsorbates. Broad multiphonon-like features dominate the TOF spectra, in both systems, and neither discrete frustrated translations, nor frustrated rotational modes are observed. Two contributions are apparent in the Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra, suggesting that there are at least two CN species in the CN@super -@/Cu(001) system. One has horizontal alignment, the other shows no preferred spatial orientation. The NEXAFS measurements from the CH@sub 3@CN/Cu(001) system suggest that there is only one type of adsorbate species, showing no preferred orientation. The lack of orientation observed in those ordered systems can imply that the surface moieties have a considerable degree of rotational freedom. DFT calculations have predicted low rotational barriers for adsorbed CN@super -@/fcc(001) systems. We discuss the helium scattering, as well as the NEXAFS spectra and analysis, in the light of this model for the dynamic adsorbate systems.

**10:40am SS2-WeM9 Mechanisms of Isomerization and Dehydrocyclization of n-Hexane on Pt(100) and Pt(111) Surfaces Studied with Sum Frequency Generation**, *K.M. Bratlie, G.A. Somorjai,* University of California, Berkeley

Using sum frequency generation (SFG) vibrational spectroscopy the adsorption geometries and surface reactions of various C@sub 6@ hydrocarbons (n-hexane, 2-methylpentane, 3-methylpentane, and 1-hexene) on a Pt(100) single-crystal surface was investigated. The adsorptions and reactions were carried out under pressures of 1.5 Torr of C@sub 6@ hydrocarbon in the presence and absence of hydrogen (15 Torr) and in the temperature range of 300 - 450K. At 300K and in the presence of excess hydrogen, n-hexane, 3-methylcyclopentane, 2-methylpentane, and 1-hexene adsorbed molecularly on Pt(100) in flat-lying geometries. Upon heating the surface temperature to 450K, both n-hexane and 3-methylpentane underwent dehydrogenation to form a surface species in a standing-up geometry: hexylidyne. 2-Methylpentane, however, was dehydrogenated to @pi@-allyl c-C@sub 6@H@sub 9@ at 375K. Further heating of the surface hydrogenated the adsorbed molecules to hexylidyne. Adsorbed 1-hexene remained unreacted as the temperature was increased. Subsequently cooling the surface temperature to 300K returned all the flat-lying hydrocarbons. The absence of excess hydrogen impeded surface reactions. Both 2-methylpentane and 1-hexene adsorbed intact and in flat-lying geometries. 3-Methylpentane and n-hexane dehydrogenate to form metallacyclohexane and flat-lying 1-hexene. All four adsorbates remained intact as the surface temperature was increased to 450K and, afterward, decreased to 300K. On the basis of these results, the mechanisms for catalytic isomerization and dehydrocyclization of n-hexane were elucidated.

**11:00am SS2-WeM10 Alane Formation on Al(111)**, *J.-F. Veyan, Y.J. Chabal,* Rutgers University

Complex metal hydrides, such as NaAlH@sub4@,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@sub4@, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na@sub3@AlH@sub6@ to the hydrogen-rich NaAlH@sub4@, 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@sub2@ 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. Molecular hydrogen does not dissociate on pure, clean Al surfaces. However, below the desorption threshold of ~280K, atomic H interacts strongly with Al by extracting step and terrace atoms to form surface alane (AlH@sub3@). Using IR spectroscopy, we have studied Al(111) after atomic H exposure and of Ti-doped Al(111) after H@sub2@ exposure. The resulting spectra show the presence of alanes, characterized by terminal Al-H and bridging Al-H-Al termination.@footnote 1,2,3@ Preliminary experiments indicate that H@sub2@ does dissociate on Ti-doped Al(111) surfaces, again forming alanes. The evolution of these oligomers as a function of substrate temperature will be discussed. @FootnoteText@@footnote 1@ C. Liang, R. Davy, H.F. Schaefer III, Chem. Phys. Lett. 159 (1989) 393. @footnote 2@ B.J. Duke, C. Liang, H.F. Schaeffer III, J. Am. Chem. Soc. 113 (1991) 2884. @footnote 3@ M. Shen, C. Liang, H.F. Schaefer III, Chem. Phys. 171 (1993) 325.

**11:20am SS2-WeM11 Exploring Experimental Vibrational Spectra of Surface Adsorbates Using DFT Modeling**, *P. Uvdal,* Lund University, Sweden **INVITED**

Experimental vibrational spectra of small molecules adsorbed on single crystal metal surfaces are explored using DFT calculations. By combining high sensitive and high resolution (@>=@ 0.5 cm@super -1@) surface infrared spectroscopy and density functional calculations details in the spectra can be detected and analyzed. Strategies for analysis at both the harmonic and anharmonic levels are discussed. Overtone and combination modes in the absence and presence of Fermi resonances are also explored. Both cluster and extended structure calculations are utilized for investigation of the coordination site of the adsorbate on the surface. Methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces are used to show the interplay between experiments and calculations.

**12:00pm SS2-WeM13 Kinetics of NH Formation and Dissociation on Pt(111)**, *R.J. Meyer, K. Mudiyanselage, M. Trenary,* University of Illinois at Chicago

The formation and dissociation of the NH species on the Pt(111) surface has been studied experimentally with reflection absorption infrared spectroscopy (RAIRS) and theoretically with density functional theory. NH is characterized by an intense and narrow peak at 3321 cm@super -1@, which allows the NH coverage to be accurately measured with RAIRS as a function of time. This permits the kinetics of an elementary surface reaction to be measured where neither the reactants nor products desorb from the surface. The experiment is performed by first preparing a well ordered p(2x2) N layer through oxydehydrogenation of NH@sub 3@, then exposing to H@sub 2@ at low temperature. It is found that NH formation follows first-order kinetics with an activation energy of 0.23 eV, whereas the dissociation reaction follows second-order kinetics with an activation energy of 1.1 eV. Because NH is more stable on the surface than N and H, the dissociation kinetics are limited by the recombinative desorption of H2, which accounts for the observed reaction order. The simplicity of this reaction provides an unusually favourable case for direct comparison between experimental measurements and theoretical calculations of the rate constant for a surface reaction. To gain further insight into experimental results, density-functional theory calculations were performed with the VASP program using a plane wave basis set and ultrasoft pseudopotentials. Rate constants were calculated based on the ratio of vibrational partition functions of the reactant and the transition state. Results indicate that the experimentally derived barrier from an Arrhenius analysis is much lower than that found in our DFT calculations using classical transition state theory. However, invoking a tunneling mechanism for NH formation readily explains this apparent discrepancy, and using an enhancement factor derived from semi-classical theory, we find very good agreement with experiment.

# Wednesday Afternoon, November 15, 2006

## Surface Science
## Room 2002 - Session SS1-WeA

### Growth Processes on Metal and Semiconductor Surfaces
**Moderator:** A.A. Baski, Virginia Commonwealth University

**2:00pm SS1-WeA1 2D Ordered Nanocluster Arrays Growth via Threading Dislocation Pair Annihilation**, *B. Diaconescu,* University of New Hampshire, US*; K. Pohl,* University of New Hampshire
The process of growing nanostructured ordered arrays of clusters on the misfit dislocation networks of strained metallic thin films@footnote 1,2@ requires a detailed understanding of the nucleation and film-adsorbate interaction at the atomic level. In the case of sulfur adsorption on submonolayer silver films on the 0001 surface of ruthenium, the Ag's short herring bone rectangular misfit dislocation unit cell of 54Åx40Å (19x16 Ag atoms) reconstructs into a well-ordered triangular array of S filled vacancy islands 50Å apart. Atomically and time resolved measurements from our home-built variable-temperature scanning tunneling microscope reveal that the S cluster growth mechanism involves a local restructuring of the highly dynamic misfit dislocation network of Ag with the final structure free of threading dislocations. Adsorbed S atoms will preferably bind on the Ru substrate thus displacing Ag atoms and creating two-dimensional S filled Ag vacancy islands while the strain of the misfit dislocation network of Ag assures the long-range order of the vacancies. The new morphology and symmetry of the composed S/Ag/Ru(0001) system is obtained via a threading dislocation annihilation mechanism in which adjacent and opposite pairs of threading dislocations are replaced by the S filled Ag vacancy islands. The driving force of this process is the strain relaxation whose local character is shown by the conservation of the unit cell size area of 21.5nm@super2@. @FootnoteText@ @footnote 1@ K. Pohl et al., Nature 397, 238 (1999)@footnote 2@ K. Thürmer et al., Science 311, 1272 (2006)*Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

**2:20pm SS1-WeA2 Diffusion and Clustering of Ag Atoms on a Si(111)7x7 Surface**, *S. Suto, J. Osiecki, K. Takusari, H. Kato, A. Kasuya,* Tohoku University, Japan
We report here the measurements of the diffusion and clustering of silver atoms on a Si(111)7x7 surface at room temperature using scanning tunneling microscopy (STM). The 7x7 structure is made of relatively large unit cells, which consist of faulted and unfaulted triangular half unit cells (HUCs). There are intercell hopping and intracell motion of Ag atoms. Up to now, the atomistic intercell diffusion of single Ag atoms and formation process of dimers was already reported by Sobotik et al.@footnote 1@ We evaporated the Ag between 0.001ML and 0.088ML on the Si(111)7x7 surface and then observed the relaxation of deposited Ag atoms for 150 min. The intercell hopping and clustering inside the HUCs were observed. First, we discuss the hopping rates and atomistic formation process of dimer, trimer, tetramer and pentamer with the theoretical model proposed by Vasco et al.@footnote 2@ The intercell hopping rates are 1.6 x 10@super -4@ 1/s from unfaulted to faulted HUCs and 1.3 x 10@super -5@ 1/s vice versa. The cluster formation process indicates the cooperative diffusion growth; the hopping rates depend on the occupation numbers of target HUCs. Second, we present the intracell motion of dimers and trimers. Third, we discuss the initial stage of nucleation. The conformation of tetramer adjacent to monomer is very stable. The monomer doesn't jump to teteramer. The tetramer doesn't show the intracell motion and the motion may contribute clustering and stability. We discuss the significance of the intercell and intracell diffusion upon clustering and nucleation. @FootnoteText@ @footnote 1@P. Sobotik et al., Surf. Sci. Lett. 537, L442(2003).@footnote 2@E. Vasco et al., Phys. Rev. B 67, 2355412(2003).

**2:40pm SS1-WeA3 Pb on Si(111)--from Magic Clusters, Nanowires to Thin Films\***, *J.F. Jia,* The Chinese Academy of Sciences, China **INVITED**
Group IV metal Pb on Group IV semiconductor Si(111) substrate has been shown to be a very unique system in terms of epitaxy growth, in which various nanostructures such as islands with magic height and atomically flat films of novel properties have been reported.@footnote 1,2@ By controlling the Pb coverage and deposition conditions, we have achieved identical nanocluster array,@footnote 3@ nanowire array@footnote 4@ and ultra-thin films with atomic-scale uniformity.@footnote 5-7@ Our scanning tunneling microscopy and angle-resolved photoemission study reveals that quantum size effect (QSE) plays a crucial role in the formation of nanowires and thin films. In this talk, I will discuss how the QSE in this system modulates the density of states near the Fermi level and regulates

the growth, and the correlation between electronic structure modulation and oscillating superconductivity transition temperature,@footnote 5@ surface stability,@footnote 6,7@ work function and chemical reactivity.@footnote 8@ @FootnoteText@ *In collaboration with Qikun Xue, Xucun Ma, Yan-Feng Zhang, Yang Guo, S. C. Li, S.B. Zhang, E. G. Wang, Q. Niu, Z. Q. Qiu and Zhong-Xian Zhao. Supported by the Natural Science Foundation of China and Ministry of Science and Technology of China.@footnote 1@ M. Hupalo and M. C. Tringides, Phys. Rev. B65 (2002) 115406@footnote 2@ M. H. Upton et al., Phys. Rev. Lett. 93 (2004) 026802@footnote 3@ S. C. Li et al., Phys Rev. Lett. 93 (2004) 116103@footnote 4@ L. L. Wang et al., submitted to Appl. Phys. Lett.@footnote 5@ Y. Guo et al., Science 306 (2004) 1915@footnote 6@ Y. F. Zhang et al., Phys Rev. Lett. 95 (2005) 096802@footnote 7@ Y. F. Zhang et al., Surf. Sci. 596 (2005) L331@footnote 8@ X. C. Ma et al., (unpublished).

**3:20pm SS1-WeA5 LEEM Observations of Pb Growth on W(110)**, *D.B. Hoffman,* **S. Chiang,** University of California, Davis
Although surface energy considerations would suggest that Pb would grow layer-by-layer on W(110), an earlier study,@footnote 1@ using low energy electron diffraction (LEED), Auger spectroscopy, and thermal desorption spectroscopy, found Stranski-Krastanov growth. After the completion of the first monolayer, our low energy electron microscope (LEEM) observations of this system show the development of 3D Pb crystallites. For Pb deposition at substrate temperature of 200C, the islands grow together and form larger islands with quasi-hexagonal sides. After about 8ML growth, gradually raising the temperature to 325C, the Pb meltiing point, causes the crystals to melt. As they melt, the islands suddenly move to step bunches and become round. They also become smaller as the Pb desorbs from the surface. Finally, some round black islands remain, corresponding to a quasi-(4x1) LEED pattern. If the temperature is lowered below 325C, those remaining islands develop a hexagonal shape. At 425C, these desorb from the surface. For growth at 300C, there appears to be a maximum coverage, possibly resulting from the competition between Pb condensation from the vapor and desorption due to the temperature. The few observed islands typically grow on top of high density step bunches. The density of the crystallites depends on the substrate temperature. For growth at 200C, the island density is about 40 times higher than for growth at 300C, with only 3 islands apparent in a 10μm field of view at the higher temperature. @FootnoteText@ @footnote 1@ E. Bauer, H. Poppa, G. Todd, Thin Solid Films, 28, 19 (1975).

**3:40pm SS1-WeA6 Exploring Complex "Wedding-Cake" Film Morphologies: Ag/Ag(111) Epitaxial Growth**, *M. Li, P.-W. Chung, E. Cox, C.J. Jenks, P.A. Thiel,* **J.W. Evans,** Iowa State University
Ag/Ag(111) homoepitaxy constitutes a prototype for rough growth and the formation of wedding-cake morphologies due to the presence of a large Ehrlich-Schwoebel (ES) step-edge barrier inhibiting downward transport. However, systematic analysis of the temperature-dependence of these morphologies is lacking, and dispute persists regarding details of the ES barrier. Our study combines comprehensive VTSTM experiments and realistic atomistic modeling and kinetic Monte Carlo simulation of growth (neither of which was available in previous studies) in the regime of 120-200 K . We thereby selectively probe those features of the rich far-from-equilibrium film morphologies which provide the most insight into the atomistic diffusion processes and barriers controlling growth. Submonolayer island growth shapes around 180K, where the fractal growth instability is quenched but full shape equilibration is not yet achieved, already provide evidence of a non-uniform ES barrier. Detailed analysis of multilayer growth morphologies focusing on top-layer island sizes at the wedding-cake peaks provides the most sensitive assessment of the magnitude of the ES barrier. However, consistent analysis requires accounting for the effect of a transition from irreversible to reversible island formation which inhibits nucleation of top-layer islands.

**4:00pm SS1-WeA7 Fundamental Limits in the Growth of Si Nanowires**, *J.B. Hannon,* IBM T.J. Watson Research Center **INVITED**
Nanowires are promising candidates for nanoscale electronic devices, and controlling nanowire properties is a major focus of research in nanotechnology. While there have been tremendous advances in both the understanding and the engineering of nanowire properties, the mechanism by which nearly all nanowires are grown (the 'vapor-liquid-solid' or VLS mechanism) is less understood. This is all the more remarkable given the fact that VLS growth has been studied for more than 40 years. We have investigated the growth of Si nanowires under conditions in which all the critical growth parameters are strictly controlled, while growth is directly

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observed using real-time in situ electron microscopy.@footnote 1@ We find that the migration of Au during nanowire growth places fundamental limits on the shape, length, and sidewall properties of the nanowires. Our results show that the conventional picture of VLS growth is insufficient when the growth takes place under conditions in which the substrate surface cleanliness, the deposition and formation of the Au-Si eutectic catalyst droplets, as well as the Si source gas purity and background contamination levels are rigorously monitored and controlled. Surprisingly, we find that under the cleanest growth conditions, VLS growth does not result in long wires of fixed diameter with clean sidewalls. Au from the catalyst droplets coats the nanowire sidewalls, terminating VLS growth when the catalyst is consumed. In addition migration of Au from one catalyst droplet to another during nanowire growth (catalyst droplet coarsening) determines the sidewall profile. In other words, the high surface diffusivity of Au, combined with the strong tendency of clean Si surfaces to getter Au atoms, together with the conventional VLS process, results in Au-coated nanowires of limited length and variable diameter. @FootnoteText@ @footnote 1@ J.B. Hannon, S. Kodambaka, F.M. Ross, and R.M. Tromp, Nature 440 (2006) 69.

**4:40pm SS1-WeA9 In-Situ Observation of Wet Oxidation Kinetics on Si(100) Surface Via Ambient Pressure X-ray Photoemission Spectroscopy**, *M. Rossi, B.S. Mun,* Lawrence Berkeley National Laboratory; *Y. Enta,* Hirosaki University, Japan; *C.S. Fadley, P.N. Ross, Z. Hussain,* Lawrence Berkeley National Lab. & UC Davis
The initial stages of silicon water-based oxidation kinetics have been investigated as a function of temperature in the hundred milli-torr pressure range using photoemission spectroscopy. The formation of chemically-shifted states of the Si 2p core level was monitored in real time while exposing the surface to water vapour. Measured oxide growth rates are compared to several theoretical models and confirm the existence of a threshold temperature above 400@super o@C after which growth rates are significantly higher. In addition, the observed enhancement of the oxide thickness at temperature higher than 450@super o@C is consistent with previous works reporting the hydrogen desorption on the Si surface.

## Surface Science
### Room 2004 - Session SS2+EM-WeA

### Organic Film Growth and Characterization
**Moderator:** J.N. Russell, Naval Research Laboratory

**2:00pm SS2+EM-WeA1 Organic-on-Inorganic Thin Film Deposition and Vice Versa**, *J.R. Engstrom,* Cornell University          **INVITED**
Thin films of organic materials differ fundamentally in many respects when compared to inorganic materials (metals, semiconductors and oxides). A key difference involves the presence of strong covalent/ionic bonding in the latter, whereas organic materials are often bound by rather weak dispersion forces. Another importance difference involves the methods and conditions used to assemble, fabricate and/or pattern these materials. For example, inorganic materials are often deposited at high temperatures, and patterned using aggressive subtractive techniques. Organics, on the other hand, can be deposited at very mild conditions, and can be patterned using additive techniques such self assembly. Interestingly, in many emerging technologies, fabricating robust interfaces between these two diverse classes of materials is absolutely essential, yet extremely challenging. In this talk we will present a summary of recent findings concerning the formation of two important interfaces: organic-on-inorganic and inorganic-on-organic. Concerning the former, we are currently conducting studies of the deposition of pentacene on clean and modified SiO@sub 2@ surfaces using supersonic molecular beam techniques. In this work we have focused initially on the effects of incident kinetic energy, angle of incidence and substrate temperature on both submonolayer and multilayer growth. Some of our more interesting observations include an effect of incident kinetic energy on the ratio of deposition rates observed for submonolayer vs. multilayer growth, and the presence of so-called rapid roughening for multilayer thin films. Concerning the latter type of interface, we are currently investigating the use of self-assembled monolayers (SAMs) to promote nucleation and growth of ultrathin inorganic films (TiN) via atomic layer deposition. In this work we have focused particularly on the initial nucleation regime, where we find that the SAMs affect nucleation significantly and in unexpected ways.

**2:40pm SS2+EM-WeA3 Organic Semiconductor Growth: Real-Time Observation of Growth Dynamics and Structural Evolution**, *S.M. Kowarik,* University of Oxford, UK, Germany; *A. Gerlach, S. Sellner, F. Schreiber,* Universitaet Tuebingen, Germany; *L. Cavalcanti, O. Konovalov,* ESRF, France
We use in-situ and real-time X-ray scattering during growth of the organic semiconductor diindenoperylene (DIP) to study the evolution of the film structure and morphology with time. Time resolved measurements in a broad q range, i.e. sampling a large number of Fourier components simultaneously, allow to directly measure (kinetically limited) growth dynamics and reveal transient structures which would be missed in post growth experiments. We identify structural and orientational transitions for the few-monolayer (ML) regime, as well as for thick (several 10's of ML) films. We show that the differences in the interaction of DIP with the substrate change the thickness as well as temperature range of the transitions, which include (transient) strain, subtle changes of the orientation, as well as complete reorientation. These effects should be considered rather general features of the growth of organics, which, with its orientational degrees of freedom, is qualitatively different from growth of inorganics. @FootnoteText@ S. Kowarik et al., Physical Review Letters, 96, 125504 (2006).

**3:00pm SS2+EM-WeA4 Resonant Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: New Probes of Electronic Structure in Organic Semiconductors**, *Y. Zhang,* Boston University; *J.E. Downes,* Macquarie University, Australia; *A. DeMasi,* Boston University; *A. Matsuura,* AFOSR; *C. McGuinness,* Trinity College Dublin, Ireland; *P.A. Glans, T. Learmonth, S. Wang, L. Plucinski, K.E. Smith,* Boston University
We report the use of synchrotron radiation-excited resonant soft x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) to study the electronic structure of thin film organic semiconductors.@footnote 1@ XES directly measures the element-specific partial density of states (PDOS) in materials. When excited at a core level absorption threshold, RIXS features can be observed in the spectra, which are related to low energy excitations. The materials studied to date include a selection of metal phthalocyanines (Cu-Pc, FCuPc, VO-PC, TiO-Pc, Ni-Pc), as well as other organic semiconductor materials such as Alq3 and QAD. Our results are in excellent agreement with theory, but differ significantly from previously published results. The films were found to be highly susceptible to radiation damage. We demonstrate the ability to accurately measure states near E@sub F@, and show that previously published XES studies of organic semiconductors are dominated by beam damage effects. This application of resonant XES has important consequences for the determination of band gap energies in organic molecular systems, since it allows determination of the non-ionized electronic structure. Supported in part by the U.S. AFOSR under FA9550-06-1-0157, by the Petroleum Research Fund, and by NSF under DMR-0304960. The spectrometer system is funded by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014. Experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences. @FootnoteText@ @footnote 1@ Y. Zhang, S. Wang, T. Learmonth, L. Plucinski, A.Y. Matsuura, S. Bernardis, C. O'Donnell, J.E. Downes, and K.E. Smith, Chem. Phys. Lett. 413, 95 (2005); J.E. Downes, C. McGuinness, P.A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

**3:20pm SS2+EM-WeA5 Structure in Self-Assembled Organic Thin Films**, *S.L. Bernasek, F. Tao,* Princeton University; *Y. Cai,* Brookhaven National Laboratory          **INVITED**
In the self-assembly of long chain hydrocarbons and substituted hydrocarbons on solid substrates, three classes of interaction energies govern the self-assembly process. They are chain-chain interactions within a lamella on the surface, interactions between ordered lamellae, and interactions between the adsorbate molecules and the underlying substrate. These interactions may be dispersive, or more directed interactions such as hydrogen bonding or acid-base interactions. We examine the interaction energies in these self-assembled organic monolayers based on structural studies using molecular resolution scanning tunneling microscopy for a variety of functionalized hydrocarbon molecules. Competitive coadsorption studies, and the effects of solvent on the stability of the structures formed are examined. Long chain carboxylic acids, di-acids, esters, anhydrides, alcohols, and di-alcohols adsorbed on highly oriented pyrolytic graphite have been examined.

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4:00pm **SS2+EM-WeA7 Epitaxial Nanolayers of Organic Small Band Gap Semiconductors: Growth and Electronic Properties of Quaterrylenes on Au**, *R. Franke, C. Wagner, S. Franke,* TU Dresden, Germany; *S.C.B. Mannsfeld,* Stanford University; *F. Fritz,* TU Dresden, Germany

The understanding of the physical properties of organic thin films is of importance for their application in novel devices. Thin films grown by the Organic Molecular Beam Epitaxy technique often exhibit highly ordered layer structures. Their physical structure is usually governed by a fine balance between weak molecule-molecule interactions and a small lateral variation of the molecule-substrate interaction potential. In order to investigate the energetics of such a heteroepitaxial layer system, one has to consider large molecular domains.@footnote 1,2@ Here we report on films of large molecules, namely quaterrylene (QT) and quaterrylenetetracarboxylic-dianhydride-diimide (QTCDI), on Au(111) in UHV. These materials are especially interesting due to their long-wavelength absorption in the NIR. In our combined LEED and STM study we found a point-on-line coincident growth with flat lying molecules for the first monolayer (ML) of QT, while we observe alternating upstanding and flat lying molecules in the second ML.@footnote 3@ In contrast, the arrangement of the QTCDI molecules in the first ML differs strongly, due to the presence of the substituents. We will also show that our experimental results correspond nicely to potential energy calculations on large ordered QT and QTCDI domains. The electronic properties of these ultrathin films were investigated by Scanning Tunneling Spectroscopy. In case of QTCDI we found a HOMO-LUMO gap of 2.1 eV, while we obtained 2.5 eV for the smaller QT. The comparison to absorbance measurements on mica allows us to estimate the exciton binding energies. @FootnoteText@ @footnote 1@ S.C.B. Mannsfeld and T. Fritz, PRB 93 (2004) 075416.@footnote 2@ S.C.B. Mannsfeld, K. Leo, and T. Fritz, PRL 94 (2005) 056104.@footnote 3@ R. Franke, S. Franke, S.C.B. Mannsfeld, C. Wagner, T. Dienel, and T. Fritz, APL 88, (2006) 161907.

4:20pm **SS2+EM-WeA8 One-Dimensional Supramolecular Assemblies on Stepped Surfaces: What Makes Them Extend into the Mesoscale Length Regime?**, *J. Schnadt,* University of Aarhus, Denmark, Sweden; *E. Rauls, Wei Xu, J. Knudsen, R.T. Vang, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

On perfect single crystal surfaces small organic molecules can self-assemble to form ordered one- and two-dimensional networks based on hydrogen bonding and other non-covalent interactions (see, e.g., Ref. 1). Such networks can grow very large and extend into the meso- and macroscale length regimes. Most real surfaces of interest, however, are afflicted with defects such as monatomic steps. These defects typically hinder the formation of large-scale networks. We show here for a particular example that it is possible to overcome this obstacle by choosing the right combination of surface and organic molecule. In the present case we investigated the self-assembly of 2,6-naphthalene-dicarboxylic acid (NDCA) on a stepped Ag(110) surface and compared it to the self-assembly of the same molecule on the Ag(111) and Cu(110) surfaces. The STM and XPS results show that NDCA on Ag(110) forms macroscopic-scale one-dimensional and directional structures across the step edges with maximum lengths in the micrometer range, notwithstanding the stepped character of the surface. This stands in contrast to the other surfaces, where the step-crossing behaviour is not observed. The experimental results together with density functional theory calculations show that the primary driving force for the formation of these long one-dimensional assemblies is hydrogen bonding, and that these bonds form also at the Ag(110) step edges. The bond formation across the step edges is driven by a combination of different factors, including the strength and bond directionality of the hydrogen bonds, the assembly directionality mediated by the substrate, and a sufficient flexibility of the adsorbate molecular backbone. A subtle balance of these factors, which depends on the particular adsorbate and the particular substrate, is required to achieve the observed step-edge tolerance of the assembly. @FootnoteText@ @footnote 1@ J. V. Barth, G. Costantini, and K. Kern, Nature 437, 671 (2005).

4:40pm **SS2+EM-WeA9 Controlled Self-Organization of Nanodots at Organic p-n Heterojunctions**, *E. Barrena, D.G. de Oteyza,* Max-Planck-Institut fuer Metallforschung, Germany; *J.O. Osso,* Institut de Ciencia de Materials de Barcelona, Spain; *S. Sellner, H. Dosch,* Max-Planck-Institut fuer Metallforschung, Germany

*Many organic devices like Light-Emitting Diodes (OLEDs), solar cells or ambipolar transistors rely on p-n junctions of organic semiconductors. Although numerous studies have been devoted to the characterization and optimization of the performance of p-n organic-based devices, the present-day knowledge on the physical principles of the growth of organic heterostructures is still poor. By combining atomic force microscopy with surface-sensitive X-ray diffraction, we have been able to get a detailed in-situ insight into the microscopic processes which take place during the growth of p-conducting di-indenoperylene (DIP) molecules onto n-conducting copper-hexadecafluorophtalocyanine (F16CuPc) thin films. We demonstrate the self-organization of well-ordered DIP nanodots with high crystallinity and show that their growth is intimately related to a novel type of interface reconstruction of the underlying F16CuPc film which affects three monolayers adjacent to the organic p-n interface. This self-organized nanopatterning of an organic p-n-junction opens new possibilities for organic electronic functions.

## Surface Science
## Room 2002 - Session SS1-ThM

### Reactivity of Oxide Surfaces I
**Moderator:** M.A. Henderson, Pacific Northwest National Laboratory

**8:00am SS1-ThM1 Interaction of Gold Atoms and Clusters with Color Centers on the Surface of MgO(001) Thin Films**, *M. Sterrer, T. Risse,* Fritz-Haber-Institute of the Max-Planck-Society, Germany; *G. Pacchioni,* University of Milano-Bicocca, Italy; *H.-J. Freund,* Fritz-Haber-Institute of the Max-Planck-Society, Germany

Catalytic activity of metal clusters may strongly be influenced by the properties of the underlying oxide support. The Au/MgO system has emerged to a prototype example in this respect because of the possibility for charge transfer from surface trapped electron centers (color centers) to adsorbed metal atoms and clusters, thus forming negatively charged metal particles. In this contribution, experimental results on the properties of single gold atoms nucleated on regular as well as color center containing MgO(001) surfaces will be presented and compared with calculated data. Electron Paramagnetic Resonance (EPR) spectroscopy and low-temperature (5K) Scanning Tunneling Microscopy (STM) has been applied to characterize single gold atoms, as well as color centers formed by electron bombardment, on the surface of MgO(001) thin films. The interaction of Au atoms and clusters with surface color centers has been monitored with infrared spectroscopy using CO as a probe for the charge state of gold particles. For single atoms and small clusters adsorbed onto color centers the observed redshift of the CO stretching frequency in comparison to CO adsorbed on neutral Au clusters is indicative for negatively charged entities. However, an even larger redshift is observed for CO on single Au atoms adsorbed on regular MgO sites. The origin of this unusual behavior will be discussed.

**8:20am SS1-ThM2 Calcium Adsorption on MgO(100): Calorimetric and Structural Studies**, *C.T. Campbell*, J.F. Zhu, N. Ruzycki, University of Washington

The adsorption of Ca on the MgO(100) surface at 300 K has been studied using microcalorimetry, in combination with LEED, AES, ISS, work function and sticking probability measurements. The sticking probability of Ca on MgO(100) at 300 K is unity. The growth of Ca on MgO(100) follows the Stranski-Krastanov mode (i.e, 2D growth and thereafter followed by 3D islands). No ordered structure can be found in LEED during Ca adsorption. Initially, Ca adsorbs cationically at defect sites (~ 6% of the surface) with a high heat of adsorption (~ 425 kJ/mol). After these sites fill, Ca grows to complete the first layer with a heat of adsorption of 167 kJ/mol. Afterwards, it grows 3D islands and its heat approaches that of Ca's bulk heat of sublimation (179 kJ/mol). Ion sputtering of the MgO surface generates O vacancies which adsorb Ca with a heat of ~350 kJ/mol.

**8:40am SS1-ThM3 Probing of the Surface Chemistry and Binding Modes of DL-proline on TiO@sub2@(110) Single Crystal Surface: A Study via High Resolution X-ray Photoelectron Spectroscopy and Temperature Programmed Desorption**, *G.J. Fleming,* The University of Auckland, New Zealand; *K. Adib, J.A. Rodriguez,* Brookhaven National Laboratory; *M.A. Barteau,* University of Delaware; *H. Idriss,* The University of Auckland, New Zealand

The use of titanium metal as a biomaterial has become common place in modern medicine due to its desirable mechanical properties and the relative chemical inertness.@footnote 1,2@ This has lead to the use of titanium in many medical applications ranging from hip replacements to aiding in the healing of fractures that occur in teeth and bones. When the titanium implant is placed inside the body's aqueous environment an oxidation process occurs, where an oxide layer forms in the range of approximately 10-100 nm thick. This layer is crucial since it prevents the Ti metal from further reacting with the biological molecules. However, it is the nature of the interaction of the bio-molecule with this thin TiO@sub2@ surface which ultimately determines the molecules final conformation. In this work we discus the surface chemistry and the nature of the interactions of DL-proline, a major constituent of the main structural protein in the body collagen I, on both oxidised and reduced TiO@sub2@(110) single crystal surfaces using High Resolution X-Ray Photoelectron Spectroscopy (HR-XPS) and Temperature Programmed Desorption (TPD). Upon adsorption on to the oxidised surface at 300 K, the N 1s spectrum revealed that proline is present as two distinct species: molecular (-NH-) and zwitterionic proline (-NH@sub2@@super+@-). Via

the use of variable temperature XPS, the zwitterionic species was found to be only weakly adsorbed and removed form the surface by approximately 600 K. On the reduced surface, an increase in the amount of zwitterionic species adsorbed to the surface was found and can be attributed to the loss of bridging oxygen atoms from the (110) surface. TPD experiments show a very complex reaction pathways, in particular on the reduced surfaces, similar in nature to previous studies performed on the TiO@sub2@(011) surface.@footnote 3@. @FootnoteText@@footnote 1@F.H Jones, Surf. Sci. Rep. 2001 42, 75. @footnote 2@B. Kasemo, Surf. Sci. 2002, 500, 656 @footnote 3@G.J. Fleming and H. Idriss, Langmuir, 2004, 20, 7540.

**9:00am SS1-ThM4 Density Functional Study of the Dissociative Adsorption of Formic Acid on the TiO@sub 2@ Rutile (0 1 1) Surface**, *P.R. McGill, H. Idriss,* University of Auckland, New Zealand

Titanium dioxide is used or present (as a consequence of oxidation of a titanium metal surface) in a range of applications, such as catalysts and medical implants, where its interaction with small adsorbed molecules is of considerable interest. While a number of studies have been conducted in this area, the majority of these have focused on the rutile (1 1 0) surface. The rutile (0 1 1) surface and its interaction with adsorbed species, while being the subject of a number of practical investigations, has until recently been neglected by computational studies. LEED evidence@footnote 1@ suggests that the (0 1 1) surface undergoes a 2x1 reconstruction as opposed to being bulk-terminated. Recently, a computational study@footnote 2@ has proposed a model for this 2x1 surface, and shows it to have several unique features such as Ti=O double bonds. In this work, periodic density functional calculations employing the PBE exchange-correlation functional and plane wave basis sets,@footnote 3@ are carried out on the adsorption of formic acid to the bulk-terminated and 2x1 models of the TiO@sub 2@ (0 1 1) surface. The 2x1 model is found to be more reactive, producing larger adsorption energies. A variety of interactions are possible for formic acid. Dissociative modes are considered because of the many experimental results which show their stable presence at room temperature. The acidic proton is thus assumed to transfer to a surface oxygen, while the remaining formate species interacts through its oxygens with one surface titanium in a monodentate or chelating fashion, or two surface titaniums in a bridging fashion. Stable conformations are found for the bridging and monodentate configurations. @FootnoteText@ @footnote 1@L. E. Firment, Surf.Sci. 116, 205 (1982)@footnote 2@T.J. Beck, A. Klust, M. Batzill, U. Diebold, C. Valentin, A. Selloni, Phys.Rev. Lett. 93, 036104 (2004)@footnote 3@Calculations performed using PWSCF, by S. Baroni, S. de Gironcoli, A. dal Corso, P. Giannozzi.

**9:20am SS1-ThM5 Structure and Catalytic Activity of Model Oxide Systems**, *O. Bondarchuk, Z. Zhang,* University of Texas at Austin; *J. Kim,* Pacific Northwest National Laboratory; *J.M. White,* University of Texas at Austin; *B.D. Kay, **Z. Dohnalek**,* Pacific Northwest National Laboratory
**INVITED**

The rutile form of titania, and particularly the [110] surface has become the prototypical substrate for studies of model system metal oxide surface chemistry. We combined atomically resolved imaging and ensemble averaged techniques to examine the adsorption, dissociation, and partial oxidation of alcohols on TiO@sub 2@(110) and (WO@sub 3@)@sub 3@/TiO@sub 2@(110) model catalysts. On clean TiO@sub 2@(110) the images obtained from the same area before and after adsorption show that alcohols adsorb preferentially on oxygen vacancies and that their dissociation occurs via O-H bond scission. The dynamics of proton diffusion was examined as a function of alcohol coverage. Model (WO@sub 3@)@sub 3@/TiO@sub 2@(110) systems were prepared using direct sublimation of WO@sub 3@ and characterized using high resolution Scanning Tunneling Microscopy, X-ray photoelectron spectroscopy and N@sub 2@ physisorption. Reactivity studies of this system towards alcohol dehydration and formaldehyde polymerization have been carried out in an ensemble averaged manner using molecular beam scattering and temperature programmed desorption techniques. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

# Thursday Morning, November 16, 2006

**10:00am SS1-ThM7 Point Defect and Adsorbate Identification on TiO@sub 2@(110) by Non-Contact AFM**, *J.V. Lauritsen*, G.H. Olesen, M.C. Christensen, University of Aarhus, Denmark; *A.S. Foster*, Helsinki University of Technology, Finland; *M. Reichling*, University of Osnabruck, Germany; *F. Besenbacher*, University of Aarhus, Denmark

The AFM can provide atomic-scale insight into the surface structure of in principle any type of oxide. In order to apply AFM to study surface chemistry it is essential to understand the contrast patterns associated with surface defects and adsorbates. This is not trivial, since the atomic contrast is determined by interactions between the surface and the tip which is mostly in an undefined state. In this study, we successfully identify defects and adsorbates present on a reduced TiO@sub 2@(110) surface under UHV conditions by means of atom-resolved non-contact AFM images and theoretical simulations. We make use of the fact that we can image the TiO@sub 2@ surface with two well-defined tip states characterized by different short-range interactions reflecting a negatively or a positively charged tip, respectively. The details of the complementary images for the two types of tip allow us to unambiguously identify the Ti@super 4+@ and O@super 2-@ sub-lattices and hence investigate the exact structure and location of defects on the metal oxide surface. A detailed statistical analysis of atom-resolved AFM images shows that three different types of defects can be seen in the first hours after sample preparation. Interestingly, the same defects are imaged either as holes in the oxygen rows or as protrusion located between the Ti rows depending on the tip charge. By comparing the characteristic contrast patterns with detailed AFM simulations for both tips, we provide a qualitative and quantitative interpretation of the AFM images, including the identification of the three types of defects as bridging oxygen vacancies and two types of bridging hydroxyls (OH) resulting from water dissociation, respectively. The observation that the AFM tip can be functionalized in situ to discriminate between chemically different elements of an oxide surface is interesting and may provide an attractive method to perform adsorbate identification on other interesting metal-oxide systems.

**10:20am SS1-ThM8 H@sub 2@O Dissociation and Proton Diffusion on TiO@sub 2@(110)**, *Z. Zhang*, O. Bondarchuk, J.M. White, University of Texas at Austin; *B.D. Kay, Z. Dohnálek*, Pacific Northwest National Laboratory

Rutile TiO@sub 2@(110) is a leading model oxide surface for the investigation of defect-related surface chemistry. The TiO@sub 2@ - H@sub 2@O system is of particular interest for both fundamental and applied science. We employed in situ Scanning Tunneling Microscopy (STM) to examine the adsorption and dissociation of water on bridge-bonded oxygen vacancies (BBO@sub v@) of the TiO@sub 2@(110) surface. Provided the H@sub 2@O coverage (< 2.5%) is less than the BBOv concentration (~10%), atomically resolved images taken at room temperature before and after water dose confirm the titration of individual BBO@sub v@ by dissociative adsorption of H@sub 2@O. The products are two hydroxyl species, one positioned at the BBO@sub v@, denoted OH@sub v@, and the other, denoted OH@sub b@, formed by protonation at either of the two nearest-neighbor bridging oxygen atoms. The protons formed by water dissociation are observed to diffuse along the BBO row. Surprisingly, the probability of OH@sub b@ diffusion is ~10 times higher than that of OH@sub v@, demonstrating their inequality. 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.

**10:40am SS1-ThM9 Water Adsorption from Submonolayer to Multilayer Coverage on TiO2(110) and Fe2O3(0001) by In Situ Spectroscopy**, *G. Ketteler*, Chalmers University of Technology, Sweden; *S. Yamamoto*, Stanford Synchrotron Radiation Laboratories; *H. Bluhm*, LBNL; *T. Kendelewicz*, Stanford University; *K. Andersson*, Stanford Synchrotron Radiation Laboratory; *D.E. Starr*, LBNL; *G.E. Brown Jr.*, Stanford University; *A. Nilsson*, Stanford Synchrotron Radiation Laboratory; *M. Salmeron*, LBNL

Despite their importance in environmental, chemical and biological sciences, the bonding structure of water at interfaces in equilibrium with vapor remains poorly understood. We have studied the adsorption of water on a rutile TiO@sub 2@(110) and hematite Fe@sub 2@O@sub 3@(0001) single crystal from submonolayer to several multilayer coverage by in situ X-ray photoemission at temperatures above 270 K in the presence of vapor pressures of up to 1.5 Torr. We find that water adsorption occurs in distinct steps that are determined by the availability of surface sites for hydrogen bonding. On TiO@sub 2@(110), very acidic sites such as O-vacancy defects present in high vacuum conditions disappear

rapidly to form ~0.25 ML of OH species on bridging positions when the vapor pressure becomes larger than 10@super -4@ Torr. A similar coverage of molecular water binds strongly to these acidic sites by charge transfer from the oxygen atom of water to the hydrogen atoms of the OH group (hydrogen bonding). This acts as a nucleation site for further water adsorption on both sides along the Ti troughs. We find no indication of a hydroxylation of regular terrace sites. The enthalpy and entropy of condensation over a wide coverage range were determined by analysis of equilibrium isobars. On Fe@sub 2@O@sub 3@(0001), defects as well as regular terrace sites are hydroxylated prior to water adsorption. Water adsorption occurred for higher relative humidity than on TiO@sub 2@(110) (5x10@super -3@ vs. 10@super -6@ % RH), and most likely it is bound to terrace OH groups. Based on these findings and NEXAFS we were able to propose a structure model for the H-bonded structures that determine water adsorption on rutile(110) and hematite(0001) from submonolaye to multilayer coverage. We will correlate the affinity of oxide surfaces to react with and bind water with the acido-basic properties of different surface functionalities.

## Surface Science
## Room 2004 - Session SS2+EM-ThM

### Self-Assembled Monolayers
**Moderator:** C. Wöll, Ruhr-Universitat Bochum, Germany

**8:00am SS2+EM-ThM1 Odd-Even Effects in Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Noble Metal Substrates**, *M. Zharnikov*, A. Shaporenko, Universität Heidelberg, Germany; *J. Müller, A. Terfort*, Universität Hamburg, Germany

Self-assembled monolayers (SAMs) of selenolates can be considered as an alternative to thiolates for the functionalization of noble metal surfaces. In view of this option, we studied SAMs formed from biphenyl-substituted dialkanediselenides (CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@Se-)@sub 2@ (BPnSe, n = 1 - 6, 10, 11) on polycrystalline (111) gold and silver substrates. The SAMs were characterized by several complementary experimental techniques. Similar to the analogous systems with the thiolate headgroup, the packing density of the SAM constituents and the orientation of the biphenyl moieties in the BPnSe films exhibited a pronounced odd-even variation with the number of methylene groups in the aliphatic linker, which was opposite on silver as compared to gold. A higher packing density and a corresponding smaller inclination of the biphenyl moieties was observed for odd numbers of the methylene units in BPnSe on Au, and for even numbers of these units in BPnSe on Ag. The observed odd-even effects are explained by the strong dependence of the bending potentials in the metal-Se-C bond on the deviation of the respective angle from an optimal value of about 104° for Au and about 180° for Ag. The optimal metal-Se-C angles are presumably determined by the hybridization of the selenium in the metal-selenolate bond, which seems to have sp@super 3@ hybridization on Au and an sp hybridization on Ag, respectively.

**8:20am SS2+EM-ThM2 Structure and Stability of Acene-SAMs**, *D. Kaefer*, G. Witte, A. Bashir, Ruhr-University Bochum, Germany; *P. Cyganik*, Institute of Physics Krakow, Poland; *J. Mueller, A. Terfort*, University Hamburg, Germany; *Ch. Woell*, Ruhr-University Bochum, Germany

In addition to tailoring mechanical and chemical surface properties self-assembled monolayers (SAMs) have also attracted significant interest in connection with studies on molecular electronics or as contact primers for organic electronic devices. The high electrical conductivity required for the latter applications has favoured the use of aromatic SAMs which generally reveal a more complex ordering mechanism as compared to aliphatic SAMs. While an improved ordering has been achieved by using additional alklyl-units within the backbone this in turn reduces the conductivity and increases the band gap of the molecular film. Recently, we have demonstrated for the case of anthracene-2-thiol that also well ordered SAMs with a completely conjugated backbone can be prepared on Au(111).@footnote 1@ In the present study we have further varied the anchoring group and prepared also an anthracene-2-selenol SAM. Here we present a comprehensive multi-technique study (based on XPS, NEXAFS, TDS, STM and LEED measurements) on the formation, molecular structure and thermal stability of both acene-based SAMs on gold. Interestingly, a remarkably improved long-range ordering and a somewhat reduced thermal stability is obtained for the anthracene-2-selenol SAM. The different films were also analyzed theoretically in the frame of DFT calculations and the microscopic interactions and energetics of both films

are compared and discussed. @FootnoteText@@footnote 1@D. Kaefer et al., J. Am. Chem. Soc. 128, 1723 (2006).

**8:40am SS2+EM-ThM3 A Survey on the Structural Properties of Alkanethiols Self Assembling on Au(111)**, *E. Barrena, C. Munuera, C. Ocal,* Instituto de Ciencia de Materiales de Madrid, Spain **INVITED**

The potential application of Self-Assembled Monolayers (SAMs) in different fields of both science and technology has motivated a large number of studies in recent years. It has become clear that the design of films with specific controlled properties requires a better understanding of the parameters governing the self-assembling process. Without doubt Alkanethiols (SH-(CH@sub 2@)@sub n-1@-CH@sub 3@ on Au(111) are the archetypal systems among SAMs. They posses important characteristics as stability, structural simplicity and well-defined order, which make them ideal for understanding the role that the fundamental interactions play in determining the self-assembled structure. In spite of their simplicity, a rich spectrum of structures has been reported. In this talk I will present a survey on the structural properties of Alkanethiols on Au(111) mainly focused on the submonolayer regime. I will show that molecular configurations consisting of molecules presenting different tilt angles and periodicities are formed for submonolayer coverage with an extraordinary degree of order. Experimental studies carried out by combining Atomic Force Microscopy and X-ray diffraction measurements will be presented showing different aspects on their growth, structure, stability including chain length dependent investigations.

**9:20am SS2+EM-ThM5 The Electronic Structure and Polymerization of a Self-Assembled Monolayer**, *D. Feng, D. Wisbey,* University of Nebraska-Lincoln*; Y. Tai,* Universit@um a@t Heidelberg, Germany*; Y. Losovyj,* Louisiana State University*; M. Zharnikov,* Universit@um a@t Heidelberg, Germany*; P. Dowben,* University of Nebraska-Lincoln, U.S.A

Although organic adsorbates and thin films are generally regarded as "soft" materials, the effective Debye temperature, indicative of the dynamic motion of the lattice normal to the surface, can be very high, e.g., in the multilayer film formed from [1,1'-biphenyl]-4,4'-dimethanethiol (BPDMT).@footnote 1@ The effective Debye temperature, determined from core level photoemission from the all carbon arene rings, is comparable to that of graphite, and follows the expected Debye-Waller behavior for the core level photoemission intensities with temperature, but this is not always the case. (We associate this rigidity to the stiffness of the benzene rings, and the ordering in the ultrathin multilayer molecular thin film.) We find that a monomolecular film formed from [1,1â?T;4â?T,1'-terphenyl]-4,4'-dimethanethiol deviates from Debye-Waller temperature behavior and is likely caused by temperature dependent changes in molecular orientation.@footnote 2@ Intermolecular Ï?-Ï? lateral interactions for [1,1â?T;4â?T,1'-terphenyl]-4,4'-dimethanethiol (TPDMT), were evident from the considerable dispersion of the TPDMT molecular orbitals with changing the wave vector k. The highest occupied molecular orbitals hybridize to electronic bands, with a band dispersion of about 300 to 400 meV. The wave vector dependence is consistent with a lateral spacing of about 5.1 @Ao@, found in STM. We also find evidence for the increase in dielectric character with cross-linking in spite of the decrease in the HOMO-LUMO gap upon irradiation of TPDMT. The cross-linking processes are also accompanied by changes in molecular orientation. @FootnoteText@@footnote 1@D.Q. Feng, R. Rajesh, J. Redepenning and P.A. Dowben, Applied Physics Letters 87 (2005) 181918 @footnote 2@D.-Q. Feng, D. Wisbey, Y. Tai, Ya. B. Losovyj, M. Zharnikov and P.A. Dowben, J. Phys. Chem. B 110 (2006) 1095-1098.

**9:40am SS2+EM-ThM6 Kinetics and Mechanism of Displacement in 1-Adamantanethiolate Self-Assembled Monolayers**, *H.M. Saavedra, C.M. Barbu, T.J. Mullen, V.H. Crespi, P.S. Weiss,* The Pennsylvania State University

We have investigated the kinetics of solution-phase displacement of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using Fourier transform infrared-external reflectance spectroscopy (FTIR-ERS) and scanning tunneling microscopy (STM). The displacement reaction can be divided into three regions: a fast insertion and nucleation of small n-dodenathiolate islands around defects in the 1-adamantanethiolate monolayer; an island growth regime in which the rate of growth is dependent on the perimeter of the island; and a final slow ordering of the n-dodecanethiolate domains leading to denser and more crystalline n-dodenathiolate domains. A study of displacement as a function of concentration revealed that the full displacement of 1-adamantanethiolate monolayers has a [n-dodecanethiol] x time@super 2@ dependence. An analytical model has been derived to describe the

displacement process, and using this model a rate constant has been determined.

**10:00am SS2+EM-ThM7 High Thermal Stability of Cross-Linked Aromatic Self-Assembled Monolayers: New Pathways for Nanopatterning by Selective Desorption**, *A. Turchanin, M. El-Desawy, A. Gölzhäuser,* University of Bielefeld, Germany

Molecular structures with high thermal stability are very desirable for applications in nanoscience and nanotechnology. We report on the thermal stability of cross-linked aromatic self-assembled monolayers (SAMs) on gold surfaces. Cross-linked monolayers were formed by low-energy electron irradiation of biphenylthiol SAMs. The pristine and the cross-linked monolayers were heated in ultra high vacuum to temperatures from 300 up to 1000K and then analyzed by X-ray photoelectron spectroscopy (XPS). We found that the pristine SAM desorbs at 400K, which is accompanied by a breaking of C-S bonds. Despite a similar C-S bond cleavage of cross-linked SAMs in the same temperature range, their carbon matrix shows a high thermal stability and remains on the surface up to 1000K. We present a detailed analysis of the temperature transformations in pristine and cross-linked SAMs on the basis of XPS data. Using a stencil mask to locally cross-link the SAMs, it is then shown by scanning electron and atomic force microscopy that after the temperature treatment monomolecular sheets of aromatic molecules, corresponding to irradiated areas in the SAM, persist at the surface. This opens a new pathway for nanopatterning by the selective desorption of non-cross-linked regions on a e-beam patterned monolayers and for technological applications of SAM coatings.

**10:20am SS2+EM-ThM8 In-situ Studies of Protein Resistance of Oligo(Ethylene Glycol) Self-Assembled Monolayers**, *M. Skoda,* Oxford University, UK*; F. Schreiber,* Universit@um a@t T@um u@bingen, Germany*; J. Willis, R. Jacobs,* Oxford University, UK*; R. Dahint, M. Grunze,* University of Heidelberg, Germany*; M. Wolff,* ESRF, France

The structure of the interface between organic matter, such as self-assembled monolayers (SAMs), and water is currently subject of intensive studies due to its importance for the understanding of surface-solvent and surface-surface interactions.@footnote 1,2@ Our focus here are OEG-terminated SAMs which are used to make surfaces resistant to protein adsorption. We report our recent results from a combined Neutron Reflectivity (NR) and Polarisation Modulated (PM) Fourier Transform Infrared Spectroscopy (FTIR) study. The PM technique enables us to address the local interaction of water with OEG groups, and is ideally complementary to NR. Our data suggest a rather strong interaction of water molecules with the EG section of the SAM, potentially the penetration of water into the SAM. Also, the measurements reveal changes in the structure of water and the protein solution in the vicinity of the SAM upon changes in temperature. Our combined NR and IR investigation helps to shed light on the problem of the subtle interactions at the organic solid-liquid interface. The benefit of using IR along with NR is also that we are more sensitive to the defect structure of the organic interface, which has an impact on the interaction with water. @FootnoteText@@footnote 1@F. Schreiber, J. Phys.: Cond. Matter 16 (2004) R881 @footnote 2@D. Schwendel et al., Langmuir 19 (2003) 2284

**10:40am SS2+EM-ThM9 Thiol-Modified Diamondoid Monolayers on Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, *T.M. Willey,* Lawrence Livermore National Laboratory*; J.D. Fabbri,* Stanford University*; J.R.I. Lee,* Lawrence Livermore National Laboratory*; P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina,* Justus-Liebig University Giessen, Germany*; J.E. Dahl, R.M.K. Carlson, S.G. Liu,* MolecularDiamond Technologies*; T. van Buuren,* Lawrence Livermore National Laboratory*; N.A. Melosh,* Stanford University

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 highly desirable properties similar to hydrogen-terminated diamond surfaces. 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 field emitters in molecular electronics, as seed crystals for diamond growth, or in other nanotechnological applications, and fundamental studies of the properties of these molecules are a necessary precursor. We have investigated the effects of thiol substitution position and polymantane order 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 both the location of the thiol and the diamondoid used. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

## Surface Science
## Room 2002 - Session SS1-ThA

### Reactivity of Oxide Surfaces II
Moderator: Z. Dohnalek, Pacific Northwest National Laboratory

2:00pm **SS1-ThA1 Effect of Pt on Clean and Oxidized Surfaces of (Ni, Pt)@sub3@Al**, *F. Qin,* Iowa State University; *J.W. Anderegg, C.J. Jenks,* Ames Laboratory; *C. Jiang, B. Gleeson,* Iowa State University; *D.J. Sordelet,* Ames Laboratory; *P.A. Thiel,* Iowa State University
We have used experimental techniques (XPS, AES, LEED LEIS and STM) and a theoretical technique (DFT) to investigate the clean and oxidized surfaces of ternary (Ni, Pt)@sub3@Al single crystals. Regarding the clean surface, our experiment results indicate that Pt segregates to the surface. Density functional calculations in the dilute limit confirm that Pt segregation is favored energetically. Regarding the oxidized surface, we systematically examined the amount, chemical nature, and spatial distribution of the oxide that forms upon saturation at oxygen pressures in the range of 10@super-8@ to 10@super-6@ Torr, as a function of oxidation temperatures (300 to 900 K) and as a function of Pt content. We found that the predominant oxide between about 300 and 700 K is NiO, covered by a thin top layer of aluminum oxide, whereas between 700 and 900 K the predominant oxide is aluminum oxide. Pt exerts four effects: (a) Pt decreases the maximum amount of NiO; (b) Pt shifts formation of Al@subx@O@suby@ to lower temperatures; (c) Pt decreases the maximum amount of Al@subx@O@suby@; and (d) Pt slows the oxygen adsorption on the clean surface.

2:20pm **SS1-ThA2 The Hydrogen Cycle on the CeO@sub 2@ Surface**, *M. Watkins,* University College London, UK; *A.S. Foster,* Helsinki University of Technology, Finland; *A.L. Shluger,* University College London, UK
The ability of Cerium atoms to exist in varying charge states permits facile surface oxidation/reduction allowing ceria to mediate oxygen concentration when part of a mixed metal oxide catalyst. There is an extensive literature on the reduction/oxidation behaviour, however, experimental conditions and uncertainties in sample preparation make interpretation of experimental data difficult. We present density functional calculations implementing the generalized gradient approximation (GGA) and on site coulomb interactions (GGA+U) on the most stable surface of Ceria, specifically focusing on its interactions with hydrogen and water. Our calculations allow us to consider the process of surface reduction and the probable state of lightly reduced surfaces in the presence of water, allowing insight into surface processes in a variety of conditions. Several interesting properties of the Ceria surface are brought to the fore - the dissociation of water molecules on the ideal surface, the rapid dissociation of water at vacancy sites and the strongly exothermic dissociation of H@sub 2@ on the ideal surface. These results have strong implications for the interpretation of experimental data, and the construction of reaction schemes for this technologically important metal oxide surface.

2:40pm **SS1-ThA3 Microscopic Studies on Dynamic Processes on Metal Oxide Surfaces Relevant to Oxide Catalyses**, *K. Fukui,* Tokyo Institute of Technology, Japan **INVITED**
Scanning probe microscopy (SPM) has great potential to understand site specific surface processes while preparation of catalysts and the role of surface defects in chemical reactions, which are key issues for developing metal oxide catalyses. In this talk, I will review our SPM studies on CeO@sub 2@(111) and Al@sub 2@O@sub 3@/NiAl(110) surfaces. CeO@sub 2@ is used for catalysts, fuel cells, etc., and their high oxygen transport and storage capacities are important for the applications. By using noncontact atomic force microscopy (NC-AFM), we have succeeded in visualizing various kinds of surface oxygen defects and highly mobile oxygen atoms around metastable multiple defects that are not reconstructed for stabilization.@footnote 1@ Activation energy for hopping of the mobile surface oxygen was estimated to be about 30 kJ mol@super -1@ from the consecutive SPM imaging of a slightly reduced CeO@sub 2@(111) at 300-400 K. We have also observed high reactivity of oxygen atom facing to the oxygen defect for extraction of hydrogen atom from the methoxy intermediate. We have been applying nonvolatile precursors for preparation of catalyst model surfaces. Water solution of [Rh(OAc)@sub 2@]@sub 2@ is ejected through a pulse-valve to a well ordered Al@sub 2@O@sub 3@/NiAl(110) under ultrahigh vacuum. By slowly annealing the precursor- adsorbed surface to 493 K, the Rh precursor decomposed and homogeneous metal clusters that contain 2-4

Rh atoms were observed by STM. It can be explained by decomposition kinetics of the precursor molecules. Finally, I will briefly introduce chemical identification of surface intermediates by using a single 'molecular tip' that can be switched by external light irradiation.@footnote 2@ @FootnoteText@ @footnote 1@ K. Fukui, S. Takakusagi, R. Tero, M. Aizawa, Y. Namai, and Y. Iwasawa, Phys. Chem. Chem. Phys. 5, 5349-5359 (2003).@footnote 2@ D. Takamatsu, Y. Yamakoshi, and K. Fukui, J. Phys. Chem. B 110, 1968-1970 (2006).

3:20pm **SS1-ThA5 Oxidation of NiAl(111)**, *E. Loginova, F. Cosandey, T.E. Madey,* Rutgers University
Our research is focused on faceting of Al@sub 2@O@sub 3@/NiAl(111) and is motivated by the possibility that alumina thin-film-covered NiAl facets might be used as oxide templates for transition metals in heterogeneous catalysis. We have performed a series of experiments aimed at understanding the adsorption of oxygen and oxygen-induced faceting of NiAl(111) using LEED, AES, SEM, AFM and high-resolution soft XPS (HRSXPS, by means of synchrotron radiation at NSLS). The atomically rough NiAl(111) surface remains planar at room temperature when exposed to oxygen. However, the oxygen-covered surface changes its morphology and becomes faceted upon annealing at 1100K and higher; nucleation and growth of nanoscale {110} facets are observed. The adsorption and reaction of oxygen are characterized by HRSXPS measurements of Al 2p and Ni 3p core levels for the faceted and planar surfaces. Moreover, after prolonged exposure to oxygen at elevated temperatures unusual three dimensional features exhibiting three-fold symmetry erupt from the surface and are oriented along low index directions; their dimensions are several micrometers in length, and 250 to 400nm high. A SEM X-ray EDS mapping study indicates that these are spinel (NiAl@sub 2@O@sub 4@) structures. A proposed qualitative model of spinel formation is as follows: when the oxygen-covered surface is annealed to elevated temperatures, oxygen diffuses below the surface and aluminum oxide nanoclusters may nucleate together with neighboring Ni-rich regions. Upon further annealing, a subsurface nucleation of NiAl@sub 2@O@sub 4@ spinel takes place at the Al@sub 2@O@sub 3@/Ni interface. Lattice strain is relieved by eruption of the spinel structures above the surface.

3:40pm **SS1-ThA6 Substrate-controlled Limiting Thickness for Nanoscale Alumina Film Growth on Single Crystal Nickel Aluminides under non-UHV Conditions**, *J.A. Kelber, N.P. Magtoto, M. Jain, C. Vamala,* University of North Texas
Nanothin ordered alumina films exposed to H@sub 2@O at partial pressures above UHV reach limiting thicknesses governed entirely by the structure of the nickel aluminide substrate (NiAl(110) vs. Ni@sub 3@Al(110)). This work provides a basis for developing quantitative predictive models of the Mott-Cabrera mechanism, and also indicates that such nanothin films have important differences from bulk oxides in non-UHV environments. Auger, LEED, and STM were used to characterize alumina films grown on single crystal substrates in UHV, and exposed to 10@super -7@ Torr < pH@sub 2@O < 10@super -3@ Torr/300 K in an adjacent environmental chamber. Film thickness was characterized by Auger spectroscopy. Films grown on NiAl(110) reach a limiting thickness of 17±1 angstroms independent of initial thickness or roughness, while films grown on Ni@sub 3@Al(110) displayed a limiting thickness of 12± 1 angstroms. The different thicknesses correspond to different energies for transfer of an Al atom from the substrate into the oxide, with the larger number of Ni-Al bonds for Ni@sub 3@Al leading to a higher barrier on that substrate. The implications of these results for ultrathin alumina films as model catalyst supports and in nanoelectronics will be discussed.

4:00pm **SS1-ThA7 NOx Storage Capacity and Thermal Aging of BaO/theta-Al2O3/NiAl(100) Model Catalyst**, *J. Szanyi, E. Ozensoy, C.H.F. Peden,* Pacific Northwest National Laboratory
NOx storage behavior of a BaO/Î¸-Al2O3/NiAl(100) model catalytic system during NO2 adsorption was studied via X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) techniques; and compared to that of the Î¸-Al2O3/NiAl(100) support material and a thermally-aged BaO/Î¸-Al2O3/NiAl(100) model catalyst at 1100K. At T > 300 K, adsorbed NO2 is converted to nitrates on all of the surfaces studied. Nitrates that are residing on the alumina sites of the model catalyst surfaces are relatively weakly bound and typically desorb within 300 K-600 K, leading to NO(g) evolution; while nitrates associated with the baria sites are significantly more stable and desorb within 600 K- 850 K, resulting in NO(g) or NO(g)+O2(g) evolution. NOx uptake by the baria sites of the BaO/Î¸-Al2O3/NiAl(100) model catalyst surface was found to be as high as a

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factor of five with respect to that of the Î¸-Al2O3/NiAl(100) support material. Thermal aging of a BaO/Î¸-Al2O3/NiAl(100) model catalyst surface at 1100 K prior to NOx uptake experiments, brings about a significant (70 %) reduction in the NOx storage capacity of the model catalyst surface.

**4:20pm SS1-ThA8 Molecular Understanding of NOx-Storage-Reduction Catalysts: NO2 and H2O Adsorption on BaO/theta-Al2O3/NiAl(100)**, *E. Ozensoy, J. Szanyi, C.H.F. Peden,* Pacific Northwest National Laboratory
NOx storage-reduction (NSR) catalysts were introduced very recently as an alternative way to treat NOx emissions originating from diesel mobile sources that are operating with high air to fuel ratios where traditional three way catalysts fail to perform. Unfortunately current understanding of NSR technology is mostly based on the industrial combinatorial studies which are focused on the product development rather than the fundamental molecular aspects of these interesting systems. Therefore here in this work, we present the very first detailed surface science study on the NSR systems where BaO nanoparticles deposited on an atomically ordered Î¸-Al2O3 ultrathin film grown on a clean NiAl(100) surface, is used as a model catalyst to mimic the industrial counterpart. BaO growth behavior on Al2O3/NiAl(100) was studied using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and low energy electron diffraction (LEED). Chemical and catalytic behavior of the BaO/Al2O3/NiAl(100) system is also investigated using H2O and NO2 as probe molecules in comparison with the clean Î¸-Al2O3/NiAl(100) surface. Preliminary results indicate that BaO deposition on Î¸-Al2O3/NiAl(100) at 300 K results in three dimensional BaO clusters which tend to wet the alumina surface upon heating up to 800 K. At higher temperatures (i.e. within 800-1200K), BaO desorption from the surface as well as interdiffusion of Ba into the Al2O3 lattice is observed. TPD studies indicate that NOx storage capacity of the BaO phase is significantly higher than that of the Al2O3 support. Our XPS and TPD data reveals that in the BaO phase, NOx is stored in the form of nitrates (NO3-) and nitrites (NO2-) that are stable up to 850 K. Co-adsorption of H2O and NO2 on BaO/Al2O3/NiAl(100) and Î¸-Al2O3/NiAl(100) surfaces was also studied using TPD to address competition for the different adsorption sites in NSR catalysts.

**4:40pm SS1-ThA9 Oxygen-induced Surface Structures of Nb(110) Studied by LEED, AES and STM**, *B. An, S. Fukuyama, K. Yokogawa,* AIST, Japan
Nb has attracted a great attention as a superconductive material and a hydrogen storage material; however, the material performance of Nb is extremely sensitive to surface oxides. Thus, the interaction of oxygen with Nb surface has been extensively studied by LEED-AES, XPS and EELS. Recently, we have studied the clean and oxygen-induced surface structures of Nb(100)[1] and Nb(111)[2] by STM with atomic resolution. In this study, we present the surface structures of Nb(110) formed during thermal cleaning in UHV and oxidation in low-pressure oxygen at 300 and 900 K by combined LEED, AES and STM. A quasi-periodically arranged sticklike structure, and the (3x1)-O, c(6x2)-O and clean (1x1) structures are sequentially observed on the Nb(110) surface at atomic resolution during thermal cleaning in UHV at temperatures from 1970 to 2500 K. At 300 K, the clean (1x1) surface is sequentially oxidized into the c(6x2)-O and (3x1)-O structures and the amorphous oxides in oxygen. At 900 K, the clean (1x1) surface is sequentially oxidized into the c(6x2)-O and sticklike structures in oxygen. The c(6x2)-O and (3x1)-O structures result from oxygen chemisorption and the sticklike structure results from the epitaxial growth of NbO@sub x@ oxide on Nb(110) surface. Atomic models for these oxygen-induced structures and the atomic-scale oxidation processes of the Nb(110) surface at 300 and 900 K are discussed. @FootnoteText@ @footnote 1@ B. An et al., Phys. Rev. B 68, 115423 (2003).@footnote 2@ B. An et al., 13th International Conference on Scanning Tunneling Microscopy/Spectroscopy and Related Techniques (STM2005), Abstracts, Sapporo, Japan, July 3-8, 2005, p. 81.

## Surface Science
## Room 2004 - Session SS2+NS+TF-ThA

## Tribology
**Moderator:** J. Krim, North Carolina State University

**2:00pm SS2+NS+TF-ThA1 Investigation of the Tribology of Diamondlike Carbon and SAMs using Molecular Dynamics**, *J. Harrison, P. Mikulski, G. Gao, J. Schall,* United States Naval Academy **INVITED**
Examination of the Tribology of DLC and SAMs using Molecular Dynamics@footnote 1@ The development of micron-sized devices, such as microelectromechanical devices, for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Amorphous carbon films, diamondlike carbon, and self-assembled monolayers (SAMs) are all possible candidates for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern both friction and wear. Over the past several years, we have performed extensive molecular dynamics simulations using the REBO@footnote 2@ and the AIREBO@footnote 3@ potentials aimed at understanding the atomic-scale mechanisms of friction in hydrocarbon systems. We have examined the contact forces present at the interface of a nominally flat, DLC tip and model alkane SAMs during sliding. We have also examined the effects of tip roughness on the contact friction. In addition, we have done simulations that have analyzed the tribological, mechanical, and transport properties of amorphous carbon films and diamondlike carbon films with various compositions. Some of our recent results will be discussed. @FootnoteText@ @footnote 1@ This work was supported by The Air Force Office of Scientific Research under contracts F1ATA04295G001 and F1ATA04295G002 (The Extreme Friction MURI) and by The Office of Naval Research (N00014-06-WX-20205).@footnote 2@ D. W. Brenner, Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B., and Sinnott, S. B., J. Phys. C. 14, 783 (2002).@footnote 3@ S. J. Stuart, Tutein, A. B., and Harrison, J. A., J. Chem. Phys. 112, 6472 (2000). .

**2:40pm SS2+NS+TF-ThA3 Interfacial Force Microscopy of Viscous Water on Hydrophilic Surfaces**, *M.P. Goertz, R.C. Major, X.-Y. Zhu,* University of Minnesota*; J.E. Houston,* Sandia National Laboratories
The hydration of surfaces is important to many fields and its effect on system behavior has been studied for decades, yet the detailed origins of the forces involved are still under debate. We use interfacial force microscope (IFM) to measure the viscosity of water thin films with nanometer thickness on hydrophilic surfaces, including silica and carboxylic acid terminated alkanethiol self-assembled monolayers. We obtain the viscosity from this interfacial water from three different measurements: shear force measurement for a water meniscus formed between a tip and the hydrophilic surface under ambient conditions; shear force measurement for the interfaces under water; and repulsive, draining-force measurements of the two approaching interfaces immersed in water. In all three types of measurements, we obtain effective viscosities more than 10@super 6@ times greater than that of bulk water for interfacial separations on the nanometer scale. The experiments clearly show that the extent of the interphase layer and its level of viscosity depend sensitively on the strength of hydrophilic interaction, gradual degrading after the surfaces have been in water for a couple of hours. Thus, it is clear that a strong water/surface interaction gives rise to an increases in water-water bonding near the two surfaces and it is this increased level of bonding that is disturbed by the lateral tip motion resulting in the observed viscosity increase.

**3:00pm SS2+NS+TF-ThA4 Design of Environmentally Friendly Lubrication Systems through Surface Grafting of Ultrahydrophilic High-density Polymer Brushes**, *A. Takahara, M. Kobayashi,* Kyushu University, Japan*; K. Ishihara,* The University of Tokyo, Japan*; A. Suzuki, M. Kaido,* Toyota Motor Co., Ltd., Japan
The hydrophilic polymer brushes of poly(2,3-dihydroxypropyl methacrylate) (poly(2)) and poly(2-methacryloyloxyethyl phosphorylcholine) (poly(3)) were prepared by surface-initiated atom transfer radical polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (1) and (3) on the initiator- immobilized silicon wafer. A large water contact angle hysteresis was observed for poly(2). Extremely low water contact angle and low contact angle hysteresis of poly(3) against water were observed. Neutron reflectivity measurements at water/poly(3) brush interface reveled that the poly(3) is highly stretched to the bulk water phase. Frictional properties of the poly(2) and (3) brushes were characterized by sliding a glass ball probe on the polymer brush surfaces in various solvents under the load of 0.49 N at a sliding velocity of 90 mm/min. Friction coefficient of poly(3) brush was lower than that of poly(2) in water. This can be ascribed to the presence of phosphorylcholine in poly(3). Further low friction coefficient was observed, even in air, by sliding a poly(3) brush immobilized glass ball against poly(3)-immobilized silicon wafer.

**3:20pm SS2+NS+TF-ThA5 Mechanical Properties of Alkanethiol Monolayers on Gold: A Force Spectroscopy Approach**, *G. Oncins, C. Vericat, F. Sanz,* University of Barcelona, Spain

Since the discovery of the self-assembling process of alkanethiol molecules on gold, these monolayers have been a matter of increasing interest not only from the point of view of basic surface science, but also due to their many applications in nanotechnology.@footnote 1@ Their mechanical properties have been widely studied by several techniques, especially by scanning probe microscopy.@footnote 2@ The growth mechanism of these monolayers on gold in vacuum has been followed by in situ Scanning Tunnelling Microscopy (STM).@footnote 3@ Atomic Force Microscopy (AFM) has proved to be suitable to study the topography and mechanical properties of alkanethiol monolayers under compression.@footnote 4@ In this contribution, we used Force Spectroscopy to study the behavior of alkanethiol monolayers deposited on a (111) monocrystalline gold surface in an electrolyte aqueous solution. The analysis of the force curves shows that the tip indents the monolayer in a stepped way and that the force at which these stepped events have place depends on the compactness of the monolayer. Thanks to newly developed models to calculate the mechanical constants of monolayers on hard substrates,@footnote 5@ we were able to calculate the different values of Young's modulus for alkanethiol monolayers of different compactness and chain length. @FootnoteText@ @footnote 1@J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, Chem. Rev., 2005, 105, 1103.@footnote 2@R.W. Carpick, M. Salmeron, Chem. Rev., 1997, 97, 1163.@footnote 3@G.E. Poirier, Langmuir, 1999, 15, 1167.@footnote 4@E. Barrena, C. Ocal, M. Salmeron, J. Chem. Phys., 2000, 113(6), 2413.@footnote 5@E.K. Dimitriadis, F. Horkay, J. Maresca, B. Kachar, R.S. Chadwick, Biophys. J., 2002, 82(5), 2798.

**3:40pm SS2+NS+TF-ThA6 Observations of Microslip in Realistic Microscopic Contacts with Combined Nanoindentation and Quartz Microbalance**, *B. Borovsky,* St. Olaf College*; A. Booth,* Grinnell College

For emerging technologies such as micromachined devices, it is increasingly important to understand the frictional properties of microscale sliding contacts and how these may be optimized with ultrathin lubricant films. While high sliding speeds and multiple contact points characterize realistic systems of interest, most theoretical and experimental studies of small contacts do not access this physical regime. We have therefore used a combined indenter probe and quartz crystal microbalance (QCM) to study the contact between a sapphire sphere and a polycrystalline gold electrode undergoing transverse shear at speeds near 1 m/s. The contacts were lubricated with monolayer octadecanethiol films. We find that both the elastic and dissipative components of the interaction are best described by the microslip model for reciprocating interfaces. We directly observe a 60% reduction in the tangential stiffness as the interface undergoes a spontaneous transition from stuck to slipping. For a mostly-slipping interface, the frequency and bandwidth shifts of the QCM are proportional to each other and track changes in the contact radius, as derived from the normal contact stiffness. Furthermore, we observe shear loss tangents over 0.4, more than 100 times larger than expected for no-slip conditions. We will show that our results are consistent with force-equilibrium microslip theory@footnote 1,2@ by proposing a simplified dynamic model of hysteresis effects in microslip, based on the driven harmonic oscillator. Research supported by NSF, Research Corporation, and Hysitron, Inc. @FootnoteText@ @footnote 1@R. D. Mindlin, W. P. Mason, T. F. Osmer, and H. Deresiewicz, Proceedings of the First U. S. National Congress of Applied Mechanics, 1951, pp. 203-208.@footnote 2@K. L. Johnson, Contact Mechanics, Cambridge University Press, NY, 1985, pp. 216-230.

**4:20pm SS2+NS+TF-ThA8 The Effect of Filling and Temperature on the Mechanical Responses of Carbon Nanotubes**, *S.-J. Heo,* S.B. Sinnott, University of Florida

It is well known that carbon nanotubes (CNTs) have fascinating electrical, optical, chemical, and mechanical properties that differ from the properties of macroscale carbon materials such as graphite or diamond. As a result of these properties, CNTs are being considered as candidate materials for MicroElectoMechanical System (MEMS)/NanoElectroMechanical System (NEMS) components. It is therefore worthwhile to study the mechanical behavior of CNTs to better understand how they might fit in with the mechanical property requirements of MEMS/NEMS. To facilitate this better understanding, we have explored two different mechanical responses of CNTs, to bending and compression, using classical molecular dynamics simulations. The second generation reactive bond order potential is used to model the short-range covalent interactions and a Lennard-Jones potential is used to model the long- range van der Waals interactions. In particular, we have modeled a three-point bend test to explore the mechanical responses of the single walls CNTs, single-walled CNTs filled with C60, double-walled CNTs, and triple-walled CNTs. A compression test has also been done on these same systems. Filling the single-walled CNTs, or increasing the number of inner shells in the case of multi-walled CNTs, is predicted to increase both the bending strength and the maximum buckling force. We have also investigated the effect of temperature on the mechanical responses of the CNTs. On the whole, higher temperatures are predicted to lower the bending strength of the CNTs. This work is supported by the National Science Foundation funded Network for Computational Nanotechnology (EEC-02288390).

**4:40pm SS2+NS+TF-ThA9 Assessing nanomechanical properties and nanoscratch resistance of Me-ZrN and ZrN thin films using Atomic Force Microscope**, *D.M. Mihut, J. Li, S.R. Kirkpatrick,* University of Nebraska-Lincoln*; S. Aouadi,* Southern Illinois University*; S.L. Rohde,* University of Nebraska-Lincoln

The present study aims at getting a better understanding of the correlation between nanomechanical properties (nanohardness (H), elastic modulus (E), H/E and H3/E2 ratio) and nanotribological properties (resulting from nanoscratch measurements) for three groups of Me-ZrN thin films (Inconel-ZrN, Cr-ZrN and Nb-ZrN) and ZrN thin films. Nanomechanical and nanotribological properties for Me-ZrN and ZrN thin films deposited by DC unbalanced magnetron sputtering were investigated using atomic force microscope (AFM) interfaced with a Hysitron Triboscope. The elastic recovery of thin films under a normal load applied during nanoindentation was evaluated and correlated with elastic recovery of thin films under a dynamic load applied during nanoscratch measurements and with other mechanical properties in order to predict the thin film composition that will better serve for wear resistant applications.

## Surface Science
## Room 3rd Floor Lobby - Session SS-ThP

### Surface Science Poster Session

**SS-ThP1 The Study of the Silicon Oxide Growth Modes with Ambient-Pressure X-Ray Photoelectron Spectroscopy**, *B.S. Mun*, Lawrence Berkeley National Laboratory; *Y. Enta,* Hirosaki University, Japan; *M. Rossi,* Lawrence Berkeley National Laboratory; *K. Lee, S.-K. Kim,* Seoul National University, Korea; *P.N. Ross,* Lawrence Berkeley National Laboratory; *C.S. Fadley,* Lawrence Berkeley National Lab. & UC Davis; *Z. Hussain,* Lawrence Berkeley National Laboratory

The growth rates of silicon oxide and the nature of the chemical bonding at the oxide interface have been investigated at ambient pressures of oxygen and water up to 1 torr in real time. The growth rates of silicon oxidation at various substrate temperatures and gases pressures of oxygen and water have been monitored. In the case of oxygen (a dry oxidation process), the growth rate of oxide is very rapid up to the thickness of one monolayer and this is followed by a second fast regime up to ca. 2 nm oxide thickness, after which the reaction rate slows considerably. In the case of water (a wet oxidation process), the growth rates of oxide become significantly slower compared to the dry process. Qualitative theoretical modeling is presented to explain the difference between dry and wet oxidation processes.

**SS-ThP2 Cathodoluminescence Degradation of $SiO_2$@:Ce,Tb Powder Phosphors Prepared by a Sol-Gel Process**, *O.M. Ntwaeaborwa*, *H.C. Swart, R.E. Kroon,* University of the Free State, South Africa; *P.H. Holloway,* University of Florida

Auger electron spectroscopy (AES), cathodoluminescence (CL) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to study degradation of the CL intensity of $SiO_2$:Ce,Tb powder phosphors prepared by a sol-gel process. The AES and CL data were collected simultaneously when the powders were irradiated for 10 hours with a beam of electrons of energy 2 keV and a current density of 54 $mA/cm^2$ in an ultra high vacuum chamber containing either $1 \times 10^{-8}$ or $1 \times 10^{-7}$ Torr $O_2$. A decrease of CL intensity during electron beam bombardment occurred simultaneously with desorption of oxygen from the surface, i.e. there is a correlation between the degradation of CL intensity and desorption of oxygen. The AES and XPS data suggest that a non-luminescent oxygen-deficient layer of $SiO_x$ (x<2)was formed on the surface and resulted in the decrease of CL intensity. The formation of the $SiO_x$ layer is consistent with an electron stimulated surface chemical reaction (ESSCR) model. Mechanisms by which oxygen desorption leads to a reduction of the CL intensity are discussed.

**SS-ThP3 Development of an Efficient Charge Transfer Potential for the Molecular Dynamics Study of Metal-Metal Oxide Interfaces**, *B.D. Devine,* University of Florida; *A. McGaughey,* Carnegie-Mellon University; *S.R. Phillpot, S.B. Sinnott,* University of Florida

The metal-metal oxide interface poses several challenges to theoretical modeling. A molecular dynamics approach requires an expression for potential energy that captures both ionic bonding in the oxide and metallic bonding in the base metal. Changes in the electron density of atoms at the interface must also be approximated with a classical expression of charge. Electronic structure theory approaches are limited to simulations of systems with comparable lattice parameters or with a high degree of lattice strain. This work presents the development of an electrostatics potential based on the work of Streitz and Mintmire@footnote 1@ whereby the partial charge on each atom is allowed to vary with atomic positions. The charge on each atom is treated as a dynamic variable, which allows for efficient parallelization and scaling with system size. The efficiency of the parallel code allows for the simulation of systems of sufficient size to compensate for lattice mismatch through a dislocation network. @FootnoteText@This work is supported by the National Science Foundation (grant no. DMR-0426870). @footnote 1@ Streitz, F., Mintmire, J, Phys Rev. B 1994, 50, 996. @FootnoteText@ 1. Streitz, F., Mintmire, J, Phys Rev. B 1994, 50, 996

**SS-ThP5 Surface Conduction Measurement on $SrTiO_3$@ (110) by a UHV-Compatible Microprober**, *H. Bando*, *Y. Aiura,* AIST, Japan; *I. Konishi,* Ibaraki University, Japan; *A. Urata,* International Servo Data Corp., Japan; *Y. Nishihara,* Ibaraki University, Japan

$SrTiO_3$@ (110) surface shows metallic character after annealing in UHV at relatively low temperature, @<=@ 1073 K, until the surface is exposed to $O_2$@ at room temperature. The surface metallic electronic states had been confirmed by our previous work by photoelectron spectroscopy, scanning tunneling microscopy/spectroscopy, and in situ surface conduction measurement. The (110) surface has an anisotropic structure, with Ti-O chains parallel to [001]. An Ultra-High Vacuum compatible microprober was employed to assess how the structural anisotropy affects the electronic surface conduction on the $SrTiO_3$@ (110). The result was understood in terms of the arrangement of the Ti-3d orbitals.

**SS-ThP6 Comparison of the Sputter Rates of $Fe_2O_3$@, $Cr_2O_3$@, $CeO_2$@, ZnO, and $TiO_2$@, Films to the Sputter Rate of $SiO_2$@**, *M.H. Engelhard*, *D.R. Baer, T. Droubay, A.S. Lea, P. Nachimuthu,* Pacific Northwest National Laboratory

Because of the increasing technological importance of oxide films for a variety of applications, there is a growing interest in knowing the sputter rates for oxides relative to the sputter rate for $SiO_2$@, a common sputter rate reference material. To support our research programs, we have made a series of measurements of the sputter rates for oxide films that have been grown by oxygen plasma assisted molecular beam epitaxy (OPA-MBE) or pulsed laser deposition (PLD). The film thicknesses and densities of these films were measured using x-ray reflectivity (XRR). These samples were mounted in a Phi Quantum 2000 where x-ray photoelectron spectroscopy (XPS) was used to monitor composition during sputtering using a 2 keV Ar@super +@ ion beam 45° from surface normal. We find that the sputter rates of $Fe_2O_3$@, $Cr_2O_3$@, and $CeO_2$@, are all significantly slower than what is observed for $SiO_2$@. In addition to the observed sputter rates, the XPS measurements allow observation of ion beam induced reduction of the oxides. Sputter rate measurements of both anatase and rutile forms of $TiO_2$@, and ZnO will also be reported.

**SS-ThP7 The Interaction of H2O with MgO(100) as Studied with Ambient Pressure Photoemission Spectroscopy**, *D.E. Starr, G. Ketteler,* Lawrence Berkeley National Laboratory; *S. Yamamoto,* Stanford Synchrotron Radiation Laboratory; *T. Kendelewicz, G.E. Brown Jr.,* Stanford University; *A. Nilsson,* Stanford Synchrotron Radiation Laboratory; *M. Salmeron, H. Bluhm,* Lawrence Berkeley National Laboratory

Water-oxide interactions play an important role in chemical, environmental and biological systems. Even though these systems have been extensively studied, the nature of the water-oxide interface remains poorly understood. Due to its simplicity and environmental relevance, the MgO(100) surface has become a prototype for studying such interactions. However, basic issues such as molecular versus dissociative adsorption at the H2O/MgO(100) interface have not been resolved. We have utilized Ambient Pressure Photoemission Spectroscopy at beamline 11.0.2 of the Advanced Light Source to address such questions. This unique experimental set-up is capable of performing photoemission experiments in the Torr pressure range allowing measurements of the H2O/MgO(100) interface under equilibrium conditions. We will present experimental results relating to the degree of dissociation and uptake of H2O on a MgO(100) thin film grown on Ag(100) at equilibrium conditions and compare these results to the current understanding of this important prototypical system.

**SS-ThP8 Adsorption of Atmospheric Gases on Iron Oxide Surface**, *J. Baltrusaitis*, *V.H. Grassian,* University of Iowa

Iron oxides are a reactive component of air, water and soil. The adsorption of several atmospheric gases including $SO_2$@, $HNO_3$@ and $CO_2$@ as a function of relative humidity has been examined on iron oxide particle surfaces. Results from several techniques including a newly designed XPS reactor/analysis system will be presented. These studies show that adsorbed water plays an important role in the surface chemistry of iron oxide particles with these molecules.

**SS-ThP9 Thermal- and Electron-Induced Reactions on the Ru(10-10) Surface: Relevance to Extreme Ulltraviolet Lithography**, *T.E. Madey*, *B.V. Yakshinskiy, R. Wasilewski,* Rutgers University

Our goal is to provide insights into surface processes that affect the reflectivity of Ru-coated mirrors used in extreme ultraviolet (EUV) lithography applications. Thin capping layers of Ru are found to reduce

contamination and oxidation of Mo/Si multilayer reflecting optics surfaces, and extend the useful lifetime of EUV multilayer mirrors. However, reflectivities of even the Ru-coated mirrors degrade in time during exposure to vacuum background gases and EUV radiation. Several techniques, including temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and electron stimulated desorption (ESD), are used to characterize thermally-induced and electron impact-induced surface reactions of gases found typically in vacuum chambers of EUV lithography systems. We present data concerning the interaction of water and acetone vapors with clean, O-covered and C-covered Ru(10-10) surfaces. A 100eV electron beam is used to mimic excitations initiated by 13.5 nm wavelength radiation employed in EUV applications. The data show non-wetting behavior of water on the air-exposed or the carbon-covered surfaces; however, water becomes more strongly bonded to an oxygen-dosed substrate. We report on the electron-induced dissociation and desorption of water adsorbed on these surfaces at low temperature. The clean Ru surface is shown to be easily covered by carbon as a result of the thermally-induced dissociation of acetone, but this reaction demonstrates different behaviour on the preoxidized Ru. Electron-stimulated desorption of O from Ru proceeds at electron energies > 25eV. Our results may provide insights into contamination and mitigation processes that affect EUV mirror lifetimes.@footnote 1@ @FootnoteText@ @footnote 1@ T. E. Madey, B. V. Yakshinskiy, N. S. Faradzhev, N. V. Edwards, Appl. Surf. Sci. (2006), in press.

**SS-ThP10 Surface Studies of Size-Selected Molybdenum Oxide Clusters**, *M.J. Patterson, J.M. Lightstone, M.G. White,* StonyBrook University/Brookhaven National Laboratory

A cluster deposition apparatus has recently been constructed and employs a magnetron sputtering source for generating gas-phase cation clusters of pure metals and metallic compounds. Of particular interest are clusters of the transition metal oxides such as Mo@sub x@O@sub y@@super +@. Bulk molybdates are one of the most widely used selective oxidation catalysts for processes such as the conversion of methanol to formaldehyde,@super 1@ and smaller molybdenum oxide clusters, x=1-3;y=1-9, have shown activity towards CO oxidation and dehydrogenation of cyclopropane@super2@. The work reported here examines the gas-phase production of an array of molybdenum oxides clusters as a first step towards investigations of model catalysts prepared by size-selected deposition. Preliminary Scanning Transmission Electron Microscope (STEM) imaging of the Mo@sub 46@O@sub 132@@super +@ cluster deposited on amorphous carbon, shows the propensity for aggregation of these clusters as the coverage increases. Current efforts involve the use of size-selected deposition to study the size-dependent structure and reactivity of supported Mo oxide nanoclusters using thermal desorption, x-ray photoemission and STEM particle imaging. @FootnoteText@ @footnote 1@ Gai-Boyes, P.L.; Catal. Rev. Sci. Eng, 1992, 34, 1-54.@footnote 2@ Fialko,E.F.; Kikhtenko, A.V.; Goncharov, V.B., et.al.; J. Phys. Chem, 1997, 101, 8607.

**SS-ThP11 Noncontact Atomic Force Microscopic Studies on Atomic Scale Structures of TiO@sub 2@ Single Crystal Surfaces Prepared by Wet Chemical Process**, *Y. Namai, S. Miyazoe, O. Matsuoka,* Mitsui Chemicals, Inc., Japan

We succeeded in observing the atomic scale structures of rutile-type TiO@sub 2@ surfaces prepared by the wet chemical method of chemical etching in an acid solution (H@sub 2@SO@sub 4@+H@sub 2@O@sub 2@) and surface annealing at 873 K in air. We tried to perform noncontact AFM observations at 450 K, which is above a desorption temperature of molecularly adsorbed water on the TiO@sub 2@(110) surface, and could obtain the atomic scale structure of the TiO@sub 2@(110) surface prepared by the wet chemical method. The surface structure was consistent with the (1 x 1) bulk-terminated model of TiO@sub 2@(110) surface. In the noncontact AFM measurements at room temperature, however, the atomic scale structure of the TiO@sub 2@(110) surface was not observed. The TiO@sub 2@(110) surface may be covered with molecularly adsorbed water after the surface was prepared by the wet chemical method. We consider that the wet chemical method is an important method in preparing atomic scale structures of TiO@sub 2@ surfaces under atomspheric conditions.

**SS-ThP12 Photoemission Analysis with Synchrotron Radiation for Nitridation of SiO@sub 2@ Thin Film on Si(001) by Irradiation of N@super +@ Ion Beams**, *Y. Teraoka,* Japan Atomic Energy Agency, Japan*; S. Hachiue, K. Yokota, M. Tagawa,* Kobe University, Japan

Energetic atomic and molecular beams are useful for modification of ultra-thin layers in ULSI devices. The silicon dioxide overlayers on Si(001) substrates were fabricated by a rapid thermal oxidation (RTO) method. The thickness was ranging from 1.6 nm to 2.8 nm, which was estimated by ellipsometry. Nitrogen gas was discharged in a PIG-type cold-cathode plasma ion source. The ions generated in the ion source were extracted and accelerated up to a translational kinetic energy of 3 keV and focused by a pair of Einzel lens. The atomic nitrogen ions were separated from other ionic species by using a Wien filter (E x B separator). The mass-selected atomic nitrogen ion beams were decelerated and irradiated at the ultra-thin silicon dioxide overlayers on Si(001) substrates by 6.3x10@super 15@ to 2.0x10@super 16@ particles/cm@super 2@ at room temperature. Chemical bonding states of Si, O, and N atoms in the nitrogen-impinged region were analyzed via photoemission spectroscopy using high brilliance and energy-resolution synchrotron radiation of 688 eV after transferring the samples from the ion beam apparatus to the photoemission apparatus. Photoemission spectra of N-1s core level could be observed in addition to Si-2p and O-1s peaks owing to the high brilliance synchrotron radiation. It was found that the silicon dioxide overlayer and the interface were effectively nitrided even by the dose of 10@super 15@ particles/cm@super 2@ order as well as the Si(001) substrate. N-1s photoemission spectra were asymmetric and deconvoluted into four components. Consequently, they were assigned to (a) N(-Si)@sub 3@, (b) N(-SiO@sub 3@)@sub 3@, (c) SiN@sub 3@-NO-SiN@sub 2@O, and (d) O-N(-Si)@sub 2@, respectively.

**SS-ThP13 Study of Step Stability on the Fe@sub 3@O@sub 4@ (100) Surface\***, *H.-Q. Wang, E.I. Altman, V.E. Henrich,* Yale University

The atomic structure along steps on metal oxide surfaces is crucial to the growth of overlayers. Yet no experimental techniques are capable of resolving that sturcture. Ab initio calculations of step structures on metal oxides are complex and have not been reported to date. By considering both the ionic and covalent components of interatomic bonding in metal oxides, we have developed a method of predicting the relative stability of different step structures.@footnote 1@ Fe@sub 3@O@sub 4@ (magnetite) is a ferrimagnetic metal that is of interest as substrate for growing complex oxides and for spintronics applications. Our STM observations on Fe@sub 3@O@sub 4@ (100) surfaces show step edges along both [110] and [1-10] directions; the step edges are found to be straight for steps heights of 4.2 ± 0.3 Å, but alternating smooth and jagged for step heights of 2.1 ± 0.2 Å. The straight (jagged) step edges are parallel (perpendicular) to the octahedral iron rows on the upper terrace. By evaluating the coordinative unsaturation of step-edge ions and the excess charge along a step, we show that steps parallel to the octahedral iron rows on the upper terrace are expected to be more stable than those perpendicular to them, in agreement with our STM observation. This step stability criterion is found to be independent of both terrace structure and step height. @FootnoteText@ *This research is partially supported by U.S. Department of Energy Grant No. DE-FG02-00ER45844, NSF Equipment Grant No. DMR-0075824, and NSF Grant MRSEC DMR-0520495.@footnote 1@V.E. Henrich and S.K. Shaikhutdinov, Surf. Sci. 574, 306 (2005).

**SS-ThP14 Self-Assembled Monolayers as Templates to Control Electrochemical Metal Deposition**, *C. Shen,* University of StAndrews, UK*; M. Buck,* University of StAndrews, UK, United Kingdom

Tailoring electrode activity by self-assembled monolayers (SAMs) of thiols is the basis of a promising scheme to generate electrode structures. It consists of a cycle which involves SAM directed electrochemical deposition of a metal pattern and subsequent transfer to an insulating substrate.@footnote 1@ The process relies on a favourable combination of properties of SAMs, i.e., the possibility to control both adhesion and interfacial charge transfer. With the availability of techniques to pattern SAMs on length scales down to nanometers the process offers the perspective to generate small scale electrode structures in a very simple way. However, with increasingly smaller dimensions of patterns the control of structures and properties of SAMs and electrochemical metal deposition becomes increasingly demanding. Some of the key challenges are the exact control of metal nucleation on a SAM modified electrode and the minimisation of defects in those types of SAMs which serve to suppress metal deposition. We report on our studies of alkane thiols and @omega@-(4'-methyl-biphenyl-4-yl)-alkane thiols which, using electrochemical characterisation and scanning tunneling microscopy, show

how variations in the SAM structure affects metal nucleation and that a non-equilibrium annealing process substantially improves the passivating properties of thiol SAMs. @FootnoteText@ @footnote 1@ I. Thom, G. Haehner, and M. Buck, Appl. Phys. Lett. 87, 024101 (2005).

**SS-ThP15 Tuning the Exchange Reaction between a Self-Assembled Monolayer and Other Molecules by Electron Irradiation**, *N. Ballav, A. Shaporenko, M. Zharnikov,* Universität Heidelberg, Germany

The molecules comprising a self-assembled monolayer (SAM) may exchange gradually when exposed to solutions containing other molecules, which are capable to build a SAM on the given substrate. This replacement offers a route to generate a new organic surface on a substrate already supporting a SAM. The rate and extent of replacement depend on a number of parameters, including the identity of the molecular chain, chain length, degree of order, and topography/roughness of the substrate. Taking SAMs of non-substituted and @omega@-substituted alkanethiolates (AT) as test systems, we studied the effect of an additional factor - electron or X-ray irradiation. We show that, in view of the exchange process, such a treatment is especially effective at a relatively low irradiation dosage, below 1 mC/cm@super 2@. Staying under this limit and varying the dosage, we were able to change the rate and extent of the exchange reaction continuously and to a noticeable extent. In particular, in the case of a non-substituted AT SAM and -OH and -COOH substituted alkanethiols in the solution, the rate of the exchange reaction could be increased by an order of the magnitude, and about 60-70% of the primary SAM molecules could be substituted after a preliminary irradiation (it was less than 10% without the irradiation). The suggested combination of e-beam patterning and substitution reaction can be used for the fabrication of molecular gradients of any particular form with the resolution down to several nanometers.

**SS-ThP16 Tribological Properties of Micro Patterned Surface**, *M. Nakano, K. Miyake, T. Murakami, Y. Ando, S. Sasaki,* AIST, Japan

Recently, the tribological properties of micro-patterned surfaces have been investigated and it has been shown that the feature of surface can affect the friction behavior of lubricated surface. In this study, the micro-patterned surface was prepared by photorisography, plasma ethcing and evaporation of NiFe alloy on Si surface in order to investigate the effect of the surface texture on the tribological properties under lubrication condition. The size of pattern was from 10 μm to 100 μm and the depth was about 10 μm. The friction test was carried out using pin-on-plate tribometer. The normal load was varied from 10 mN to 100 mN and the sliding speed was from 1mm/sec to 10 mm/sec. The commercial lubricants and the pins made of cast iron were used. The patterned surface showed less variation of friction force with the variation of the normal load than the flat surface. Moreover, the friction force of the patterned surface became lower. On the other hand, in the case of dry condition, the friction coefficient was high and the friction behavior was independent of surface feature. Therefore, it was considered that the surface texturing affect the lubricant film thickness and the frictional behavior.

**SS-ThP17 Multivariate Analysis as an Enabling Method for Structure-to-Property Studies of Fuel Cell Electrocatalysts**, *S. Pylypenko, T.S. Olson, M. Dowlapalli, K. Artyushkova, J.E. Fulghum, P. Atanassov,* The University of New Mexico

Understanding the surface chemistry and structure of electrocatalysts, and linking structure to properties is important for optimization of catalyst performanace and elucidation of failure mechanisms. Characterization of the changes in surface chemistry that occur as a function of catalyst production, modification and aging requires identification of subtle changes in a complex system. X-ray photoelectron spectroscopy (XPS) in combination with multivariate analysis (MVA) was used to study a number of materials, including non-platinum electrocatalysts, based on pyrolysed porphyrins, and carbon blacks used as catalyst supports. Analysis of chemical bonding information from XPS spectra frequently utilizes deconvolution of the spectra into multiple peaks, resulting in significant interpretational ambiguities. Multivariate analysis techniques, in combination with conventional curve fitting, facilitate both interpretation of the data and the development of structure-property correlations. Principal component analysis (PCA) was applied to the XPS curve fit results from the catalysts and supports, enabling identification of chemical species, grouping of chemical species as a function of catalyst treatment, and correlation with electrochemical performance. The methodology applied in this study can be effectively used to identify active catalytic sites responsible for oxidation/reduction process, detect chemical species

responsible for corrosion of the catalyst material, and assist in design of optimized electrocatalysts.

**SS-ThP18 Isotope Effect in Chemicurrent Experiments**, *D. Krix, R. Nuenthel, H. Nienhaus,* University of Duisburg-Essen, Germany

During exothermic reactions of atomic hydrogen or deuterium on a silver surface hot charge carriers are produced which have been observed by using Ag/Si(111) Schottky diodes. Thin film devices provide a means to bring a charge detector as close to the reaction site as the mean free path of the charge carriers. In the case of a p-doped substrate the Schottky barrier works as a high-pass energy filter for hot holes. We have therefore produced large area Schottky diodes with film thicknesses of up to 30 nm varying the thickness to rule out any influence of this device parameter. Those diodes were then exposed to beams of hydrogen atoms and deuterium atoms produced in a hot-capillary source. Gas exposures do not affect the Schottky barrier height significantly. While exposing the samples to defined atom fluxes the closed-loop current was monitored in real time. It shows that the current is proportional to the amount of flux supplied as long as the total flux is low and sticking is independent of hydrogen coverage. We have found hydrogen to generate more than three times the amount of hot holes than are created during reactions with deuterium. Theoretical predictions of non-adiabatic energy dissipation using the electronic friction model agree well with the experimental results.

**SS-ThP19 Tunable Frequency Alternating Current Scanning Tunneling Microscope for Surface Excitation in the Microwave Frequency Range**, *A.M. Moore, P.S. Weiss,* The Pennsylvania State University

We have built a scanning tunneling microscope (STM) capable of measuring the response of surfaces excited with microwave frequencies (up to 20 GHz) at sub-nanometer resolution. Two frequencies are applied to the STM tip and the nonlinearity of the tunnel junction mixes the frequencies, generating new signals including at the difference of the frequencies applied. This ultrahigh resolution (<1 nm) profiling tool enhances and complements what is obtained through current metrology tools and will support semiconductor processing as the size scale of devices continues to decrease. It will allow us to study single molecule rotations excited at microwave frequencies and also allow us subsurface properties of thin films and cluster-assembled materials.

**SS-ThP20 Purification of Otho-Hydrogen by Adsorption Separation Method Combined with Thermal Desorption Process**, *K. Niki, T. Kawauchi, M. Matsumoto, K. Fukutani, T. Okano,* The University of Tokyo, Japan

Separation of ortho-hydrogen from normal hydrogen, a mixture of ortho H@sub 2@ (o-H@sub 2@) and para-H2 (p-H@sub 2@), has been carried out by using an adsorption separation method, which exploits the difference between the activation energies of desorption of o-H@sub 2@ and p-H@sub 2@. @footnote 1@ The optimum value of the separation coefficient S was empirically determined and analyzed based on adsorption equilibrium data of o-H@sub 2@ and p-H@sub 2@. Recently, we developed rotational state-selective thermal desorption spectroscopy (TDS) for hydrogen molecules. Grains of activated alumina were contained in a sample cell attached to the cold head of a mechanical refrigerator. After the activated alumina was exposed to normal hydrogen for a certain time, it was heated at a constant rate. The desorbing hydrogen molecules were ionized from selected rotational quantum status by resonant-enhanced multiphoton ionization (REMPI). The TDS peak temperatures were measured as 18K and 16 K for o-H@sub 2@ and p-H@sub 2@, respectively. In previous reports on the adsorption separation process, the molecular process during the desorption period was not well-analyzed. Based on our state-selective TDS data, we calculated the enhancement of the separation coefficient by sampling the desorbing hydrogen molecules at an intermediate temperature during the TDS measurement. To prove this estimation of the enhancement of the separation coefficient, we constructed an o-H@sub 2@ purifier. The apparatus consists of two parts: an adsorption separation cell system and a REMPI detector system. Details of the experimental results of o-H@sub 2@ purification and the comparison with the calculation is to be presented. @FootnoteText@ @footnote 1@ C. M. Cunningham et al., J. Am. Chem. Soc. 80, 2382 (1957).

**SS-ThP21 Energetic Gas-Phase Collisions with Alkanethiol Self-Assembled Monolayers**, *N.A. Kautz, D.P. Fogarty, S.A. Kandel,* University of Notre Dame

The combination of a molecular-beam source with an ultra-high-vacuum scanning tunneling microscope allows the investigation of structural and chemical changes of octanethiol self-assembled monolayers resulting from energetic gas-surface collisions. In situ monitoring of the sample before,

during, and after collision shows that at the molecular scale, close-packed regions of the monolayer show very few changes even when bombarded by hyperthermal or reactive species. However, defects in the organic monolayer, which result automatically from the film deposition process, result in more reactive environments in which significant changes are seen.

**SS-ThP23 Beam Damage on Drug Tablet during XPS Analysis**, *C.A.J. Kemp, X. Dong,* Eli Lilly and Company

It is a well-known phenomenon that certain samples are susceptible to beam damage during XPS analysis. Dry-formulated drug products usually contain, in addition to the active pharmaceutical ingredient (API), multiple excipients. It is of great interest to understand the potential for inadvertent sample alteration during the analysis of drug products using XPS. In the current study, the potential beam damage to a drug tablet was evaluated. The preliminary results revealed the discoloration of the analytical area on the tablet after it was exposed to a 15kV X-ray beam for 2 hours. By ToF-SIMS analysis it was found that the characteristic mass peak of the excipient mannitol was relatively lower in the spectra of the discolored area than in the spectra of the control area, when compared to the characteristic peak of API. It suggests that mannitol is more susceptible to beam damage than API under the typical XPS analysis conditions. The effect of API level, and different XPS analysis conditions on the extent of beam-induced damage will be further investigated.

**SS-ThP24 Motion of Water Droplets on Inclined Hydrophobic Surfaces in Flowing Air**, *A. Hashimoto, J.-H. Song, M. Sakai,* Kanagawa Academy of Science and Technology, Japan*; S. Suzuki,* Kanagawa Academy of Science and Technology, and Tokyo Institute of Technology, Japan*; N. Yoshida,* Kanagawa Academy of Science and Technology, and The University of Tokyo, Japan*; Y. Kameshima, A. Nakajima,* Kanagawa Academy of Science and Technology, and Tokyo Institute of Technology, Japan

Recently, not only for water-repellent treatment, control of liquid droplets on solid surfaces has become important for advanced device systems such as MEMS or microscale chemical processing. So far, various investigations have been performed to examine the motion of a liquid droplet on a solid surface using external fields such as gravity, electric fields, photo-illumination and a heat gradient. However, investigation on the control of a liquid droplet using air flow is insufficient although it is indispensable for the design of industrial items such as windshield of automobiles. In the present study, we investigated effect of air flow on droplet shape and motion on hydrophobic surfaces using high-speed cameras. Three silanes were deposited on Si substrates by CVD method. Water droplets with different weight (10 ~ 50 mg) were placed on the surfaces, which were tilted at 0, 35, 45 and 60 ° in an open-circuit-type wind tunnel. We carefully observed the droplets by high-speed cameras changing a wind velocity (0 ~ 20 m/s). The droplet motion on inclined hydrophobic surfaces in air flow was classified into three categories by the competition between the forces of the wind and the gravity; sliding down, stopping and climbing up. Detailed relationship among these behavior, moving speed, droplet deformation, experimental condition and surface state will be discussed.

**SS-ThP25 Computational Simulations on the Interaction of Water and Hydrophobic Surface**, *Y. Kameshima, S. Suzuki,* KAST and Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan*; A. Nakajima,* KAST and Tokyo Institute of Technology, Japan

Wettability is an important phenomenon of solid surfaces from theoretical, practical, and technological aspects. And the wettability of the solid surface is a characteristic property of materials and is controlled by the surface energy and roughness. If the wettability and the water repellency are simulated by the theoretical calculation, the obtained information is useful to design the hydrophobic surface. The interaction of water with hydrophobic surface was evaluated by the theoretical calculation. Molecular orbital (MO) calculations were used to determine the energy change of water molecular by their distance to typical model surface of hydrophobic coatings. Molecular dynamics (MD) calculations were used to study nanoscale water dynamics phenomenon. Clusters of C13H22 and C13F22 consisted by three hexagon of carbon were used for the model clusters for MO calculation. The water molecule was placed center of the substrate cluster. The distance of water molecule and the surface hydrogen or fluorine was set to be 1.0ï½z4.0â"«. On each system, the optimization of the structure was done so that the total energy of each system may become a minimum. As the result, the water molecule could not be separated from the surface of C13F22 cluster. CH4 and CF4 molecules in water cell were used for the typical model for MD calculation. Under 1 ns

calculations, there were no difference in radial distributions for CH4 and CF4 calculations.

**SS-ThP26 Deformation and Motion of a Droplet of Water-based Magnetic Fluid on a Hydrophobic Surface by Gravity and Magnetic Field**, *A. Nakajima,* KAST (Kanagawa Academy of Science and Technology) and Tokyo Institute of Technology, Japan*; H. Asakura,* KAST and Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; S. Suzuki, Y. Kameshima,* KAST and Tokyo Institute of Technology, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan

Control of a liquid droplet on a solid surface has attracted much attention as an indispensable technology for various industrial items, especially for hydrophobic coatings. Recently, not only for water-repellent treatment, this technology has become important for microscale chemical processing systems. To date, various investigations have been carried out to examine the motion of a liquid droplet on a solid surface using external fields. However, investigations on the control of a solid and liquid mixture using an external field are limited. Magnetic fluid is a very common solid-liquid mixture, In the current paper, motion and deformation of a water-based magnetic fluid on a hydrophobic surface were investigated under gravity and a magnetic field. Surface energy and the resultant contact angle of magnetic fluid depend on the surfactant concentration. Viscosity of the fluid is mainly governed by magnetite concentration. The front edge of the droplet moved under a weak external field. The rear edge required a higher external field for movement. The force for moving of the front edge is almost identical between gravity and the magnetic field. However, that of the rear edge is different. The motion of magnetic fluid by an external field depends on the concentrations of surfactant and magnetic particles, external field, and experimental assembly.

**SS-ThP27 Observation of Internal Fluidity in a Water Droplet during Sliding on Hydrophobic Surfaces by Particle Image Velocimetry**, *M. Sakai, A. Hashimoto, M. Sugibuchi,* Kanagawa Academy of Science and Technology, Japan*; S. Suzuki,* Tokyo Institute of Technology and KAST, Japan*; N. Yoshida,* CCR, the University of Tokyo and KAST, Japan*; Y. Kameshima, A. Nakajima,* Tokyo Institute of Technology and KAST, Japan

Recently, the importance of dynamic hydrophobicity (sliding acceleration) is recognized in various industries. In the current paper, we evaluated the sliding behavior; acceleration, advancing-receding contact angles, and the shape of water droplets on various declined hydrophobic surfaces by a high-speed camera system with motion picture analysis. The intensity of the interaction between the solid surface and liquid dominated the sliding behavior of the water droplet. Moreover, during the droplet sliding on the hydrophobic surface, the rolling like a catapillar motion and the slipping on the contact line was observed from the motion of the indicator particle in the droplet. The sliding velocity in the water droplet can be described by the two elements. The cross-section images, which were obtained by a sheet laser (wave length: 488 nm), from the center of the droplet were precisely analyzed by the particle image velocimetry. We successfully confirmed the thickness of boundary layer for the hydrophobic surface by this method. We will discuss the effect of the velocity gradient around the boundary between liquid and the hydrophobic surface on the sliding behavior of water droplets.

**SS-ThP28 Liquid Selection using Sliding Behavior of Droplets on Line-Patterned Hydrophobic Surfaces**, *A. Nakajima,* Tokyo Institute of Technology, Japan*; S. Suzuki,* KAST (Kanagawa Academy of Science and Technology) and Tokyo Institute of Technology, Japan*; K. Tanaka,* Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; Y. Kameshima,* KAST and Tokyo Institute of Technology, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan

Technologies of hydrophobic coating have been important for various industrial items. The evaluation of a solid surface's hydrophobicity is divided into two branches: static hydrophobicity and dynamic hydrophobicity. For assessing solid surfaces' dynamic hydrophobicity, information related to the speed at which the droplet can be removed from the surface at a certain tilt angle is becoming important. Surface composition patterns using self-assembled monolayers (SAMs) were fabricated recently using photolithography. Wettability on well-defined micropatterned surfaces with different surface free energy has been specifically examined, although wetting behavior of droplets on homogeneous surfaces has mainly been studied. The relationship between heterogeneous patterned surface and dynamic hydrophobicity on patterned surfaces is not precisely reported. In the present paper, we

demonstrate liquid selection effect using sliding behavior of droplets on the line-patterned hydrophobic surfaces. A cleaned Si wafer was micro-patterned by fluoroalkylsilane (FAS) and octadecyltrimethoxysilane (ODS). When a Si wafer with the patterned lines was rotated to a certain angle in plane and inclined from horizontal position, droplets of water or ethanol solution slid down on the surface with some displacement to line direction with changing their sliding velocity. This behavior depends on not only surface energy and droplet mass but also a rotation angle and patterning structure. Detailed discussion on the relationship among these factors will be presented.

**SS-ThP29 Optimization of Lithographic Parameters for Writing Thiolated Molecules via Nanografting and NPRW using an Open-Loop AFM System**, *W. Serem, J.N. Ngunjiri, J.C. Garno,* Louisiana State University

The unique advantages and capabilities of nanografting and NanoPen Reader and Writer (NPRW) for writing arrays of nanopatterns (< 200 nm) of self-assembled monolayers (SAMs) using an open-loop AFM system will be presented. Both methods apply force to an AFM tip to write SAM nanopatterns in ambient environments. Nanografting is accomplished in a dilute solution of the molecules chosen for writing. The AFM tip is scanned at high force, displacing molecules of the matrix SAM under the tip. Fresh molecules from solution assemble onto the surface following the track of the scanning tip. For NPRW, the AFM tip is coated with SAM molecules for writing in air or water. During writing, the tip is scanned at a high force to write nanopatterns within a methyl-terminated matrix SAM resist. For both methods, the resolution of writing depends on the geometry of the AFM tip, easily achieving 10 nm dimensions with standard commercial cantilevers. Nanografting and NPRW are excellent for in situ studies and use the same tip for fabrication and imaging the designed nanostructures. Both methods offer flexibility and can be used to write n-alkanethiols with different terminal chemistries and chain lengths. When using an open-loop AFM scanner, the writing speed, direction and force must be optimized to achieve high-resolution writing. Vector movements which translate the tip in both the X and Y directions simultaneously are shown to produce problems with alignment and registry for nanopatterns. We will disclose the programming strategies for tip translation which lead to improvements in the uniformity, alignment and geometries of nanopatterns written using open-loop feedback control.

**SS-ThP30 Mechanical Properties of Surfactant Aggregates at Liquid-Solid Interfaces: Molecular Dynamics Simulations**, *P. Chiu,* University of Florida*; K. Shah,* Intel Corporation*; S.B. Sinnott,* University of Florida

There are a wide range of applications that use surfactants, including dispersion in such things as paints and detergents, controlled drug delivery systems, and chemical mechanical polishing (CMP) of silicon wafers. As a result, great strides have been made in using experimental methods to shed light on the behavior of surfactants in solution and at the solid-liquid interface. Those experimental studies, however, have produced little insight into understanding the behavior of surfactants at the molecular level, the mechanics of which are still to be explored. Consequently, new developments in molecular dynamics (MD) simulation have been directed towards this area of study. This research uses MD simulations to study the mechanical properties of surfactant aggregates, specifically the surfactant dodecyltrimethyl ammonium bromide (C$_{12}$TAB), at liquid-solid interfaces, such as at water-silica and water-graphite interfaces. Indentation simulations both normal to the substrate, at an angle, and laterally are considered. The aim is to understand the failure mechanisms of micelles, if any, during nanoindentation with different proximal probe tip indenters.

## Surface Science
## Room 2002 - Session SS-FrM

### Oxide Surfaces and Interfaces
**Moderator:** S.A. Chambers, Pacific Northwest National Laboratory

**8:00am SS-FrM1 Reduction of Sn-Oxide Phases on PtSn Alloys**, *J. Kim,* Lehigh University*; S. Thomas,* University of Southern California*; **B.E. Koel,** Lehigh University*
The chemistry that occurs at oxide-metal interfaces found for metal nanoparticles on oxide supports or formed by oxidation of the metal nanoparticles themselves is important for understanding and controlling processes in heterogeneous catalysts, electrocatalysts, and sensors. For example, the origin of improved selectivity of Pt-Sn bimetallic catalysts for selective hydrogenation of unsaturated aldehydes has been attributed to the presence of cationic Sn sites. We have investigated the thermal stability, and reducibility in $H_2$ at pressures ranging from UHV to one atm., of several distinct ordered and disordered structures, monolayer and multilayer phases, of tin oxide films formed at the surface of Sn/Pt(111) and Sn/Pt(100) surface alloys. The oxide phases and the progress of their reduction were characterized using TPD, LEED, STM, AES, and high-resolution XPS. We find enormous sensitivity of the reduction of these tin oxide films on the detailed chemical nature and structure of the films. Such sensitivity can alter the thermal reduction temperature by 300 K and the reducibility in $H_2$ by many orders of magnitude.

**8:20am SS-FrM2 First Principles Studies of CO Adsorption and Oxidation on Cu2O(100)\***, *S. Stolbov, D. Le, T. Rahman,* Kansas State University
Recent experimental findings[1] indicate that the rate of CO oxidation on Cu2O surface is much higher than that on Cu and CuO surfaces. This result is also in qualitative agreement with results on copper oxide nanoparticles. To gain insight into the factors controlling the reactivity of oxide surfaces, we have examined from first principles the energetics of adsorption and oxidation of CO on Cu2O(100). Calculations are based on density functional theory using the generalized gradient approximation for the electron exchange-correlation term. Furthermore, we obtain the pressure/temperature (p,T) surface phase diagram by applying the ab initio thermodynamics approach[2] to the surface in contact with gaseous O2. We find that the O-termination of Cu2O(100) is preferred for all reasonable range of temperature and O2 pressure. We also find that CO molecules which chemisorb on the surface O, directly associate with it to form CO2 without any activation barrier. On the other hand, CO molecules which adsorb on a surface Cu atom are found to slide first towards the neighboring O atom to form CO2. We analyze the local densities of electronic states and valence charge densities of the systems to rationalize the results. @FootnoteText@ @footnote 1@T.-J. Huang and D.-H. Tsai, Catal. Lett. 87, 173 (2003). @footnote 2@K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002). * Work supported in part by DOE under grant No. DE-FG02-03ER15465 and computational resources provided by NSF Cyberinfrastructure and TeraGrid grant No; DMR050039N.

**8:40am SS-FrM3 Structure, Energetics and Reactivity of Step Edges on Anatase TiO2(101)\***, *A. Selloni,* Princeton University    **INVITED**
Defects strongly affect the physical and chemical properties of metal oxide surfaces, and step edges are the most common type of defects. On nanoparticles the high concentration of step edge atoms may even dominate surface chemistry. Atomic-scale descriptions of metal oxide step edges are scarce. We report first-principles calculations of the structure, energetics, and chemistry of step edges on the (101) surface of TiO2 anatase, an important photocatalytic material. A procedure based on systematic calculations of related vicinal anatase TiO2 surfaces has been used, which yields step edge energies with remarkable accuracy. The electronic structures of the stepped surfaces and adsorption of prototype molecules have been also investigated. The present results allow us to obtain a detailed and complete understanding of available experimental observations. In particular, predictions of step edge configurations are in excellent agreement with Scanning Tunneling Microscopy measurements. @FootnoteText@ *Work in collaboration with Xue-Qing Gong, Department of Chemistry, Princeton University; Matthias Batzill and Ulrike Diebold, Department of Physics, Tulane University.

**9:20am SS-FrM5 Nitrogen Doping of TiO@sub 2@ Single Crystals**, *M. Batzill, E.H. Morales, U. Diebold,* Tulane University
TiO@sub 2@ is one of the most widely used photocatalytic materials for photo degradation of organic pollutants, self cleaning surfaces, and photolysis of water for hydrogen production. The wide band gap of TiO@sub 2@ limits its photoactivity to UV radiation, however. For utilizing a wider spectrum of the solar light a narrower band gap would be advantageous. In a recent paper by Asahi et al.@footnote 1@ it was proposed that such a band gap narrowing can be achieved by doping TiO@sub 2@ with nitrogen. Here we present detailed photoemission and scanning tunneling microscopy studies of single crystal rutile and anatase TiO@sub 2@ samples, which were nitrogen-doped by ion implantation.@footnote 2@ Only one oxynitride species was identified in XPS for nitrogen. Valence band spectra showed additional states at the top of the valence band for N-doped samples. These were identified as N-2p states, which appear to be not strongly hybridized with the O-2p valence band of pure TiO@sub 2@. Changes in Ti-3d induced defect states within the band gap are discussed in terms of N@super 3-@ induced charge compensation processes. We conclude that N-doping lowers the O-vacancy formation energy, which also triggers a 2x1 surface reconstruction of the rutile-TiO@sub 2@(110) surface upon N-doping. @FootnoteText@ @footnote 1@ R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293, 269 (2001).@footnote 2@ M. Batzill, E.H. Morales, U. Diebold, Phys. Rev. Lett. 96, 026103 (2006).

**9:40am SS-FrM6 Growth and Properties of High-Quality Epitaxial N-doped TiO@sub 2@(110) Grown by Molecular Beam Epitaxy**, *S.H. Cheung, D.E. McCready, A.G. Joly, S.A. Chambers,* Pacific Northwest National Laboratory
N-doped TiO@sub 2@ is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. Despite a plethora of papers, typically lacking adequate materials characterization, very little is known about the fundamental properties of N:TiO@sub 2@. To this end, we have undertaken a study of TiO@sub 2-x@N@sub x@ films grown on rutile TiO@sub 2@(110) by molecular beam epitaxy. A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied using an effusion cell. Due to the interplay between substitutional N (an acceptor) and interstitial Ti (a donor), the conductivity and majority carrier type depend sensitively on the three atomic fluxes during growth. N incorporation at O sites appears to be thermodynamically limited to less than 2 at. % unless heavily defective material is deliberately made, in which case higher concentrations can be achieved. Optical absorption shows that substitutional N results in a new broad feature at the top of the valence band which functionally reduces the rutile bandgap by ~0.5 eV. The high degree of structural quality was evidenced by observations of finite thickness fringes in the vicinity of the (330) Bragg peak in high-resolution X-ray diffraction. Lattice expansions of 0.5% along the a axis and 0.8% along the c axis accompanies N substitution for O. A preliminary investigation of N-doped anatase grown on LaAlO@sub 3@(001) reveals that the same limited extent of N incorporation occurs for anatase as for rutile.

**10:00am SS-FrM7 N and C Doping in TiO2 Using Ion Implantation for Photocatalysis Applications**, *P. Nachimuthu,* UNLV*; S. Thevuthasan,* PNNL*; E.K. Vestergaard,* University of Washington*; M.H. Engelhard, I. Lyubinetsky, V. Shutthanandan,* PNNL*; T. Tyliszczak, D.K. Shuh,* LBNL*; Z. Dohnalek, M.A. Henderson,* PNNL
In semiconductor photochemistry, the redox potential of a photocatalyst is strongly influenced by its bandgap, which dictates the energy separation of the electron-hole (e@super -@/h@super +@) pairs by its band edge positions relative to electron donor/acceptor orbitals in the reactants. This in turn influences the degree of overlap between adsorbate molecular orbitals (in this case water) and the electronic states associated with the e@super -@/h@super +@ pairs. TiO@sub 2@ is one of the few candidates with promising photocatalytic properties although the optical absorption spectra of TiO@sub 2@ have poor overlap with the solar spectrum and high e@super -@/h@super +@ pair recombination rates. Solid state doping of anions causes a red-shift of the TiO@sub 2@ absorption spectrum into the visible region and visible light phtotoactivity has been observed from N-doped TiO@sub 2@. Recently, we have investigated the N and C doped in rutile TiO@sub 2@ by ion implantation. C 1s near-edge x-ray absorption fine structure (NEXAFS) shows features characteristic of Ti@sub 4@C and the intensity of these features are significantly improved following annealing at high temperatures. On the other hand, N 1s NEXAFS indicates that the features characteristic of N@sub 2@ increase with increasing annealing temperatures. XPS measurements clearly show peaks

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at 403 eV characteristic of N-N interaction and at 396 eV from N atom present in the substitutional/interstitial site. Nuclear reaction analysis (NRA) and XPS depth profile measurements show that N remains in the lattice following high temperature annealing. These results will be discussed along with the of ion implantation for applications in photocatalysis.

**10:20am SS-FrM8 STM Characterization of TiO$_2$(011)-2x1 Surface Morphology**, *O. Dulub, M. Batzill, U. Diebold,* Tulane University*; A. Selloni,* Princeton University*; C. Di Valentin,* Università degli Studi di Milano-Bicocca, Italy

Titanium dioxide has a wide range of applications where its surface properties play an important role. Therefore, their study on the atomic scale is essential. The TiO$_2$(011) surface prepared by sputtering and annealing exhibits a stable (2x1) reconstruction in agreement with a previously proposed model by Beck et al. [Phys. Rev. Lett. 93 (3) (2004) 036104]. Atomically resolved STM images of the surface reveal flat terraces separated by monatomic steps. Unlike other TiO$_2$ surfaces, the (011) surface contains one-fold coordinated Ti=O (titanyl) groups, which are expected to have a diverse effect on surface chemistry. The Ti=O species form zig-zag chains along the [01bar1] direction, with O atoms imaged bright in empty-state STM. The most frequently occurring defects observed on the surface after argon ion sputtering and high-temperature UHV annealing are point defects (oxygen vacancies) and monolayer deep holes with several atoms missing. Oxygen vacancies appear as dark spots in STM images, in good agreement with DFT calculations. The density of such defects on the surface is reduced substantially upon re-annealing in molecular oxygen. Oxygen vacancies, as well as anti-phase domain boundaries in the (2x1) structure, are reactive sites for adsorption of gas molecules. Hydrogen atoms of hydroxyls groups, formed from dissociation of either H$_2$ or H$_2$O in the residual gas, are imaged as bright spots in STM. Argon ion bombardment and subsequent annealing in oxygen results in a rough surface with some (3x1) reconstructed areas. Segregation of calcium impurities from the bulk leads to a well-ordered overlayer structure with a centered (2x1) unit cell.

**10:40am SS-FrM9 Structure and Properties of MBE-grown Epitaxial Anatase Films with Rutile Nanocrystalline Inclusions**, *R. Shao, D.E. McCready, C.M. Wang, S.A. Chambers,* Pacific Northwest National Laboratory

TiO$_2$ is a wide band-gap oxide which is of interest for photocatalytic oxidation of organic pollutants. It is known that TiO$_2$ nanoparticles, which are suspected to consist of an anatase core and a rutile shell, enhance photocatalytic reactions compared to the pure phases. It has been suggested that this phenomenon is due to enhanced electron-hole pair lifetimes associated with the spatial separation of carriers across the anatase/rutile interface due to a staggered band alignment. Fundamental insight calls for the preparation and characterization of a model system with a well-defined anatase/rutile interface. To this end, we have used a region of the molecular beam epitaxy growth phase space for TiO2 on LaAlO$_3$ (001) and SrTiO$_3$ (001) in which rutile inclusions nucleate within a continuous epitaxial anatase layer. We start by growing a pure anatase (001) layer and then change the growth conditions to drive the nucleation of rutile particles. Control of the density and size of the rutile nanocrystals is highly sensitive to the growth conditions. X-ray diffraction shows that the rutile [100] axis is normal to the film plane. The anatase/rutile interface is atomically sharp and the preferential orientations of rutile nanocrystals in the film are determined from high-resolution transmission electron microscopy. X-ray photoemission measurements for anatase, rutile and anatase/rutile composite films indicate that the interface forms a nested rather than staggered heterojunction. In this talk, we will present details of the growth and properties of this system along with a study of electron transport across the interface as measured by scanning tunneling microscopy.

**11:00am SS-FrM10 Sputtering Induced Vacancy Cluster Formation on TiO$_2$(110)**, *P. Karmakar, G.F. Liu, J.A. Yarmoff,* University of California, Riverside

Defects and oxygen vacancies markedly affect the electronic structure and adsorption properties of metal oxides, such as TiO$_2$. In addition, the catalytic behavior of supported metal particles, such as Au nanoclusters, can be enhanced by defects within the substrate. In this work, defects are introduced in a controllable manner via low energy ion bombardment, and the resultant material is probed with Scanning Tunneling Microscopy (STM) and X ray Photoelectron Spectroscopy (XPS). It is shown that 0.5 keV Ar$^+$ bombardment of TiO$_2$(110)

leads to a change of stoichiometry and the formation of mesoscopic features. XPS measurements reveal the loss of oxygen and the reduction of Ti$^{4+}$ to Ti$^{3+}$. STM reveals the formation of nanometer scale vacancy clusters. The instabilities initiated by sputtering lead to the formation of these structures. The process can be explained within the framework proposed by B. Kahng et al.[1] Following significant Ar$^+$ bombardment, the cavities extend below the surface and diffuse out when the sample is annealed. Regular rectangular holes with single atomic layer steps form when sputtered TiO$_2$ is annealed at 880° C. @FootnoteText@ @footnote 1@ B. Kahng, H. Jeong and A. L Barabasi, Appl. Phys. Lett. 78, 805 (2001).

**11:20am SS-FrM11 Atomic Structure of the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° Phase by Direct-Method Analysis of Surface X-Ray Diffraction Data**, *S.S. Parihar, H.T. Johnson-Steigelman, P.F. Lyman, V.L. Shneerson, R. Fung, D.K. Saldin,* University of Wisconsin-Milwaukee*; F.U. Renner, T.-L. Lee, J. Zegenhagen,* ESRF, Grenoble, France

Polar-terminated oxides, where the bulk stacking produces a net dipole moment perpendicular to the surface, exhibit a rich set of energy-lowering mechanisms at the vacuum interface. For example, the polar oxide surface MgO(111) is known to undergo several air-stable reconstructions, including p(2x2) and ($\sqrt{3}\times\sqrt{3}$)R30° phases. The observed periodicity depends on O partial pressure and temperature. The ($\sqrt{3}\times\sqrt{3}$)R30° phase has been the subject of several structural investigations,[1,2] but agreement has not been reached on a unique structure. We report on a structural investigation of the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° reconstruction by surface x-ray diffraction. Our direct-methods analysis[3] reveals maxima in the surface electron density. The atomic model suggested by the analysis can then be refined using the conventional $\chi^2$ process. For the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° surface, we observe 1/3 ML of adatoms, and 2/3 ML vacancies. Implications for structural models via conventional refinement will be discussed. @FootnoteText@ @footnote 1@ R. Plass et al., Phys. Rev. Lett. 81, 4891 (1998).@footnote 2@ A. Subramanian et al., Phys. Rev. Lett. 92, 026101 (2004).@footnote 3@ P. F. Lyman et al., Surf. Sci. 600, 424 (2006).

**11:40am SS-FrM12 Surface Structure of BaTiO$_3$ (001)**, *D.B. Li, R. Shao, D.A. Bonnell,* University of Pennsylvania

Although the structures of oxide surfaces have been the focus of much research for several decades, those on BaTiO$_3$ (001) have received relatively little attention. We have recently shown that this surface adopts several reconstructions depending on thermo-chemical history. The influence of ferroelectric domains on surface structure is not known. Here we use STM, nc-AFM, LEED and Auger electron spectroscopy to compare morphologies and reconstructions that form under different annealing conditions. In the evolution of a series of reconstructions a structural model, based on a comparison of STM and nc-AFM contrast of the (r5xr5)-R26.6$^o$ and (3x1) superstructures, is proposed. Differences with analogous SrTiO$_3$ surfaces will be discussed.

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