Monday Morning, November 15, 2004

Surface Science
Room 210B - Session SS1-MoM

Electronic Structure and Excitations

Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS1-MoM1 Electronic Stablization of Nanophase Separation Along Si Atomic Chains***, **J.L. McChesney**[1],* University of Wisconsin*; J.N. Crain,* NIST*; V. Perez-Dieste, F. Zheng,* University of Wisconsin*; M.C. Gallagher,* Lakehead University, Canada*; F.J. Himpsel,* University of Wisconsin

One-dimensional surface structures have received a great deal of interest both for probing the fundamental physics phenomena of low-dimensions and for applications in nano-electronics. The Si(111)5x2-Au surface exhibits one-dimensional tracks with extra Si atoms on top, which have been used to demonstrate an atomic scale memory [1] and to probe the limits of storage density by studying the effects of inter-atomic coupling [2]. Atomic-interactions play a vital role in the determination of the electronic structure and vice versa. In an effort to elucidate this connection we used angle-resolved photoemission spectroscopy to probe the relevant electronic states in the vicinity of the Fermi level EF [3]. They are located at the zone boundaries of a 5x4 unit cell which explains the 5x4 periodicity of the inter-atomic potential [2]. This corresponds to the preferred spacing of the Si adatoms while the optimum chain doping would correspond to a 5x8 arrangement of the Si adatoms [4]. We propose that the nanoscale phase separation of this surface [5] into semiconducting 5x4 and metallic 5x2 sections is a way to accommodate these conflicting requirements. 1. R. Bennnewitz et.al., Nanotech. 13, 499 (2002). 2. A. Kirakosian et.al., Phys. Rev. B. 67, 205412 (2003). 3. J. L. McChesney et.al., submitted to Phys. Rev. B. 4. S. C. Erwin, Phys. Rev. Lett. 91, 206101 (2003). 5. H. S. Yoon et.al., Phys. Rev. Lett 92,096801 (2004). @FootnoteText@ .

8:40am **SS1-MoM2 The Hammett Equation in Single Molecule Chemistry: Probing a Linear Free Energy Relationship One Molecule at a Time***, B.V. Rao, K.-Y. Kwon, A. Liu, **L. Bartels**,* University of California, Riverside

Selective addressal of specific chemical bonds inside a molecule is at the heart of modern chemistry. With the advent of low-temperature scanning tunneling microscopy (STM), specific bonds of individual molecules became accessible in a controlled manner. Here we present how this technique may be applied to the study of a fundamental pillar of physical organic chemistry, the Hammett Equation, one molecule at a time. Thiophenol and its halo/alkyl-substituted derivates adsorb on Cu(111) at 15K in a horizontal fashion leaving the thiol (-SH) group intact. Excitation by electrons of several hundred meV energy from an STM tip can induce selective dissociation of the SH-bond. This process is confirmed by STM-based vibrational spectroscopy of the S-H stretch mode. We measured the rate of electron-stimulated hydrogen abstraction for p-Fluoro-, p-Chloro-, p-Bromo-, p- Methyl-, m-Fluoro-, and m-Chloro-Thiophenol as well as for the unsubstituted species. The observed dehydrogenation rates follow the @sigma@-values of the Hammett equation, which were derived by pKs measurements on solutions of substituted benzoic acids 70 years ago. The positive @rho@ value of our measurements of 1.4 corresponds qualitatively to the solution phase value for thiophenols suggesting that a negatively-charged transition state is at the core of the STM-based hydrogen abstraction mechanism.

9:00am **SS1-MoM3 Benzene on Au{111} at 4 K: Observation of Molecular Cascades and Substrate-Mediated Interactions***, **P. Han**[2], E.C.H. Sykes, B.A. Mantooth, Z.J. Donhauser, P.S. Weiss,* The Pennsylvania State University

The role of the surface electronic structure was previously shown to have important implications on the long-range intermolecular interactions, molecular alignment and dynamics through substrate-mediated interactions (SMI) [1]. To date, attempts at quantifying SMI using scanning tunneling microscopy (STM) involve statistical measurements of STM images of static systems [2]. Here we present the study of benzene monolayer growth on a Au{111} surface using low temperature STM at 4 K. In this study, the tip-induced motion in the benzene overlayer was observed with 600 time-lapse STM images and it allowed us to statistically quantify the forces involved in SMI from a kinetic stand point. These estimates helped us explain the kinetics of the benzene motion, as well as the thermodynamics that determine the packing structure over the various regions of the reconstructed Au{111} surface. We also report the observation of tip-induced molecular cascade motion, and demonstrate that this observed motion is concerted in nature, not a result of individual random movements [3]. @FootnoteText@ [1] E. C. H. Sykes, P. Han, S. A. Kandel, K. F. Kelly, G. S. McCarty, and P. S. Weiss, Accounts Chem. Res. 36 (12), 945 (2003). [2] J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. 85 (14), 2981 (2000); N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern, Phys. Rev. B 65 (11) (2002). [3] P. Han, B. A. Mantooth, E. C. H. Sykes, Z. J. Donhauser, and P. S. Weiss, Accepted for publication by J. Am. Chem. Soc; E. C. H. Sykes, B. A. Mantooth, P. Han, Z. J. Donhauser, and P. S. Weiss, in preparation for J. Am. Chem. Soc.

9:20am **SS1-MoM4 Listening to Atom Dynamics During Atomic Manipulation***, **J.A. Stroscio**, R.J. Celotta,* National Institute of Standards and Technology

The physics of atomic manipulation with the scanning tunneling microscope (STM) involves many processes that depend on the tip-adatom interaction. We discuss our work on using atom manipulation imaging and the noise characteristics of the tunneling current as probes of the physics of the atomic manipulation process. By scanning a single Co atom across a Cu(111) surface, along the same path we would use to image the Cu surface, we can obtain a highly detailed image, showing three distinctly different atom binding sites. If the Co atom is positioned over an hcp site, dynamic behavior is observed both in the STM image and the tunneling current. The site dependent noise in the tunneling current is in the audio range and can be heard as the atom is dragged over the surface. We show that this dynamic behavior corresponds to state fluctuations of the Co atom; the Co hops between the hcp site and adjacent fcc sites. This occurs by the creation of an ideal, tunable, multi-well potential by the tip-adatom interaction. An ideal double-well potential can be created by positioning the Co atom slightly off the hcp site. Two-state transfer rates between the hcp and fcc sites are obtained by measuring the distribution of residence times in each state. The transfer rates show two distinct regimes. A transfer rate independent of tunneling current, voltage and temperature that is ascribed to quantum tunneling between the two wells, followed by a transfer rate with a strong power law dependence on current or voltage, indicative of vibrational heating. The role of these effects in atomic manipulation applications will be discussed.

9:40am **SS1-MoM5 Electronic Structure and Excitations at the Atomic Scale***, **W. Ho**,* University of California, Irvine **INVITED**

This talk will highlight the use of scanning tunneling microscopes (STM) to measure the electronic structure and elementary excitations at solid surfaces. The unique capabilities of the STM enable these measurements to be carried out with atomic resolution on single atoms, molecules, and nanostructures on solid surfaces. Electronic, vibrational, vibronic, plasmonic, and magnetic excitations will be discussed. These results provide a fundamental understanding of nanoscale properties and phenomena.

10:20am **SS1-MoM7 Quantum Well States in Thin Films of Pb on Si(111)***, **J.H. Dil**, J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; A. Mans, A.R.H.F. Ettema,* Delft University of Technology, The Netherlands*; K. Horn,* Fritz-Haber-Institute der MPG, Germany

The Pb/Si(111) system shows a rich variety of interesting physical properties and phenomena, such as the magic height of islands, vertical Friedel oscillations @footnote 1@, a competition between classical and quantum mechanical effects in the shape relaxation @footnote 2@, anomalous optical absorption @footnote 3@ and an anomalous behaviour in the Hall effect as a function of thickness. Hence it is important to study the electronic structure of thin Pb films on Si(111) with a view to understanding the origin of these phenomena. Photoemission experiments carried out at the synchrotron radiation facilities of MAX-lab in Lund (Sweden) and BESSY in Berlin, from a large range of film thicknesses prepared under different conditions exhibit clear signatures of 2 D quantum well states. Their energy dispersion with parallel electron momentum show an anomalously large in-plane effective mass of the 2D quantum well state bands, with the highest effective masses for states near the Fermi level. This contrasts with effective masses of the bulk bands from which these states are derived, and with similar data from the Pb/Cu(111) system @footnote 4@; also, band structure calculations for bulk and thin film slabs predict bands with predominantly free electron character. Our analysis suggests that this phenomenon may be due to a strong electron correlation effect in the 2D bands of the Pb quantum well states. @FootnoteText@ @footnote 1@ W.B. Jian, W.B. Su, C.S. Chang, T.T.Tsong, Phys.Rev.Lett.90, 6603 (2003). @footnote 2@ H. Okamoto, D. Chen, T.

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

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

Yamada , Physical Review Letters 89, 6101 (2002). @footnote 3@ M. Jalochowski et al., Physical Review B 66, 205417 (2002). @footnote 4@ J.H. Dil, J.W. Kim, S. Gokhale, M. Tallarida, K. Horn, PRB, in press.

10:40am **SS1-MoM8 Newns-Anderson Model for Chemicurrents**, ***S. Holloway,*** University of Liverpool, UK; *D. Bird, M. Mizielinski,* University of Bath, UK; *M. Persson,* Chalmers University of Technology, Sweden

The excitation of electron-hole pairs when a reactive species adsorbs on a surface should invariably be expected but it has proved difficult to quantify the strength of the process. We have performed first principles calculations for the interaction of a hydrogen atom with a Cu surface to investigate the chemicurrent induced. This calculation involves calculating the electronic response to the adsorbate motion and then using a forced oscillator description for the energy dissipation. Results will be presented for hydrogen and deuterium and comparison made with recent experiments. The numerical results are consistent with values derived from experiment for the H-Cu system. Application of the standard spin-polarised DFT approach results in a phase transition that occurs as the resonance intercepts the Fermi level. This, in turn, gives rise to an infinitely strong dissipative force above the metal which results in unphysical dynamics even before the atom encounters the adsorption well. The origin of the problem has been traced back to the nearly adiabatic assumption that is made in the standard application of time dependent DFT to electronic friction. In this present work, we deploy the Newns-Anderson description and show that this rather unexpected behaviour can be quite straightforwardly understood. Furthermore, we present for the first time, results for the chemicurrent using a new theoretical approach based on the time-dependent Newns-Anderson model.

11:00am **SS1-MoM9 Direct Observation of Electron Emission from a Metal Surface Due to Scattering of Vibrationally Excited Molecules**, ***J.D. White***, *J. Chen, D. Matsiev,* University of California, Santa Barbara; *D.J. Auerbach,* Hitachi Global Storage Technologies; *A.M. Wodtke,* University of California, Santa Barbara

We report the observation of electron emission from low work function metal surfaces due to the scattering of highly vibrationally excited nitric oxide (NO) molecules. Using Stimulated Emission Pumping (SEP) and Franck Condon Pumping (FCP), we prepare NO in vibrational states ranging from v=1 to v=18. SEP allows us to control explicitly the final vibrational state (from v=4 to v=18) while FCP allows us to prepare a range of states (dependent on the Franck Condon Factors) from v=0 to v=5 in the Electronic Ground State. These molecules are then scattered off of a low work function surface (~1.3 - 1.6 eV), in our case submonolayer cesium on gold, and the emitted electrons are detected with a Multi Channel Plate assembly. Our experiments indicate that the observed particles are indeed electrons which are promptly emitted after collision of the vibrationally excited NO with the surface. Vibrational energy dependence experiments suggest a threshold for emission at roughly the work function of the surface. The maximum efficiency we have measured is approximately 0.02 electrons per molecule. Possible mechanisms for vibrationally induced electron emission are discussed. Our results are very important in determining the limitations of using the Born Oppenheimer Approximation (BOA) to model highly excited gas-surface reaction dynamics. The transition state for molecular dissociation very likely involves molecules stretched to large bond distances, which can be approximated by highly vibrationally excited molecules. Experiments along this vein will help to determine how accurate it is to use the BOA for modeling these systems.

11:20am **SS1-MoM10 Co-Adsorption of Polar Molecules with SF@sub6@ on Ru(0001): Effect on Adsorption Geometry, Ion Yields and Electron-Mediated Chemistry**, ***D.O. Kusmierek***, *N.S. Faradzhev, T.E. Madey,* Rutgers, the State University of New Jersey

SF@sub6@ is widely used as an electron scavenger for high voltage applications, and is a potent greenhouse gas; the electron-induced reactivity of gaseous and condensed SF@sub6@ is an environmentally important issue. The present work focuses on the effect of polar co-adsorbates H@sub2@O and NH@sub3@ on (1) adsorption geometry of SF@sub6@ on Ru(0001) at 25K, (2) formation and desorption probabilities of ions (F@super+@, F@super-@,) generated by electron stimulated desorption (ESD) of SF@sub6@, passing through condensed overlayers, and (3) chemical reactions activated by low-energy electrons. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF@sub6@ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Deposition of a polar molecule overlayer leads to changes in both intensities and trajectories of desorbing F@super+@ and F@super-@ ions. Low-energy electron-irradiation of SF@sub6@ films causes a step-wise decomposition of the molecules, and new chemical species are detected for electron-irradiated SF@sub6@ adsorbed on water (ice) surface. Analysis of the angular distributions of F@super+@ and F@super-@ as a function of temperature, co-adsorbate coverage and electron irradiation, in conjunction with TPD data, give insight into the structure of the molecular film, the ESD mechanisms, the ion/molecule scattering processes and the radiation chemistry observed here.

11:40am **SS1-MoM11 Spin-Resolved Plasmon Dispersion of Gd(0001)**, ***H.-K. Jeong***, *D.S. Wisbey, P.A. Dowben,* University of Nebraska-Lincoln

The spin-resolved plasmon dispersion, Ep(k//), of Gd(0001) on Mo(112) was investigated using spin-polarized electron energy loss spectroscopy. In spin polarized electron spectroscopy, the spin majority band structure of Gd(0001) exhibits different electron-phonon coupling than spin minority. There is some modest indirect evidence from the effective higher Debye temperature [1] derived from the spin minority bands than from the majority bands, but the compelling evidence arises from the spin dependence plasmon structure. Spin-polarized plasmon dispersion was observed. In addition to the spin-resolved plasmon dispersion, Ep(k//), we will show plasmon energies are dependent on primary energies and temperature. [1] Hae-Kyung Jeong, R. Skomski, C. Waldfried, Takashi Komesu, P. A. Dowben, E. Vescovo, "The Effective Spin Dependent Debye Temperature of Gd(0001)", accepted Physics Letters A (2004).

Surface Science

Room 210C - Session SS2-MoM

Functionalization of Semiconductor Surfaces

Moderator: J.N. Russell, Jr., Naval Research Laboratory

8:20am **SS2-MoM1 Atomic-level Control of Chemical Properties of Si(100) with Dopant Impurities**, *Y. Wang,* ***G.S. Hwang***, The University of Texas at Austin

Atomic-level manipulation of surface chemical properties becomes necessary for the fabrication of ever smaller semiconductor devices and a wide range of future molecular devices. The electronic structure of semiconductor surfaces can be modified by surface reconstruction, defects, impurities, and adsorbates. This will in turn alter physical and chemical processes occurring on the surfaces. One could envisage atomistic control of surface reactivity by incorporating dopant impurities into the surface or subsurface. A detailed understanding of the role of dopants as possible reaction promoters or inhibitors will contribute greatly to finding a new and reliable way to construct desired organic function assembly on semiconductors for various chemical, biological, and electronic applications. Using density functional theory calculations, we have looked at the modification of Si(001) surface properties by incorporating Boron and Phosphorous atoms into the surface and subsurface layer. We have found that surface (or subsurface) dopants bring about a significant change in surface chemical properties by altering surface polarization. As a result, chemical reactions on a dopant-modified surface show a distinctively different feature from on the clean surface. In this talk, we will present i) the effect of subsurface Boron on the surface reactivity of Si(001) based on water and ammonia adsorption and ii) auto-catalyzed molecular nanostructure formation of styrene on Si(001) using Phosphorous as initiator and terminator.

8:40am **SS2-MoM2 Chemistry on Surfaces of Thin Films and at Thin Film/Silicon Buried Interface: Vinyltrimethylsilane and (hfac)Cu(VTMS) on Si(100)-2x1 and on TiCN/Si(100)**, ***A.V. Teplyakov***, *L. Pirolli,* University of Delaware

Surface chemistry of vinyltrimethylsilane (VTMS) and (hfac)Cu(VTMS) on Si(100)-2x1 surface covered with several nm thick TiCN films formed from tetrakis-(dimethylamino)-titanium has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES) and thermal desorption mass spectrometry. The structure of the films has been analyzed using time-of-flight secondary ion mass spectrometry and atomic force microscopy. This unique combination of surface analytical techniques allows one to follow chemical and physical changes at the surface of the system, within the thin film, and at the thin film/silicon interface. VTMS was found to adsorb molecularly both on Si(100)-2x1 and on the surface of the TiCN thin film at cryogenic temperatures (100 K), while it exhibits chemisorption if dosed at room temperature. Multiple reactions involving VTMS on both surfaces occur upon thermal annealing: molecular desorption around 400 K, formation and desorption of propylene by 500 K, decomposition leading to the release of silicon-containing products around 800 K. On a clean Si(100)-2x1, surface decomposition leading to the production of silicon carbide and the release of hydrogen takes place at 800 K. This chemistry is markedly different from the previously reported behavior of VTMS on Si(111)-7x7 surface resulting in 100% conversion to silicon carbide. (hfac)Cu(VTMS) chemistry, in particular the role of the VTMS ligand and the decomposition products, has also been studied both on clean Si(100)-2x1 and on a TiCN film deposited on silicon. A comparison of these studies with previous aluminum precursor chemistry will be discussed.

9:00am **SS2-MoM3 Functionalization of Semiconductor Surfaces**, *M.A. Filler, D.W. Porter,* Stanford University*; A. Kim,* KAIST, Korea*; J.A. Van Deventer, **S.F. Bent**,* Stanford University **INVITED**

The growing importance of organic materials in electronic and optical technologies motivates the development of new attachment chemistries for combining organic layers with semiconductor substrates. We have investigated methods of functionalizing semiconductor surfaces by chemically reacting organic molecules at silicon and germanium surfaces in vacuum. These surfaces present intriguing templates for chemical reactions because the nature of the (100)-2x1 reconstructed surface of silicon and germanium yields dimers that can mimic the reactivity of organic functional groups. This behavior allows for the use of a wide variety of reactions to attach organic groups to the semiconductor surface. Our studies have explored the reactivity of a range of functional groups, including alkenes and dienes, amines, alcohols, carbonyls, nitriles, and isocyanates. The results of experimental and theoretical studies of the adsorption chemistry will be described in the context of several key mechanistic themes, including electrophilic/nucleophilic chemistry and [4+2], [3+2], and [2+2] cycloaddition reactions. Approaches for using these reactions for molecular layer deposition will be introduced, and some of the challenges in organic functionalization, including formation of inter- and intradimer products as well as coverage-dependent effects, will be discussed.

9:40am **SS2-MoM5 Adsorption of Amines on Germanium and Silicon Surfaces**, *P. Prayongpan, **C.M. Greenlief**,* University of Missouri-Columbia

The bonding and structure of organic molecules with semiconductor surfaces is important for a variety of potential applications. This work examines the interactions between small organic molecules; ethylamine and allylamine, with Si(100)-2x1 and Ge(100)-2x1 surfaces. Ab initio calculations are used to investigate the transition states and predicted adsorption products for the reactions between the organic molecules and a dimer cluster model of the semiconductor surfaces. The cluster models include Si@sub 9@H@sub 12@, Ge@sub 9@H@sub 12@, and a mixed cluster; Ge@sub 2@Si@sub 7@H@sub 12@. Ultraviolet and x-ray photoelectron spectroscopy are used to examine the chemical bonding of the adsorbed products. This work will examine the effect of electron donating organic molecules with semiconductor surfaces. The selectivity and reactivity of functional groups in the surfaces will be described. According to our recent experimental and theoretical studies, the adsorption products for the interaction between amine molecules with Si(100)-2x1 and Ge(100)-2x1 surfaces are temperature dependent. Low temperature adsorption favors dative bonding of the amine with either surface, whereas different adsorption geometries are observed for adsorption at higher surface temperatures.

10:00am **SS2-MoM6 Silicon Surface Chemistry of Substituted Triazines**, ***S.M. Casey**, L.M. LeMond,* University of Nevada, Reno

Deposition of substituted triazines onto the Si(100) surface was examined in order to investigate the initial stages of an organic molecular beam epitaxial growth approach to carbon nitride film formation. These reactions were probed under ultrahigh vacuum conditions using thermal desorption spectroscopy, Auger electron spectroscopy, and low-energy electron diffraction. Experiments reveal that the reactions of species such as 2-amino-1,3,5-triazine are self-limiting with a saturation coverage of about one molecule per four silicon surface atoms. Computational modeling of available reaction pathways was also performed using ab initio and density functional theory approaches. The results from these computations using cluster models of the silicon surface are consistent with the results from the experimental studies, and point to stable reaction products where the incident substituted triazine molecule bridges between two adjacent (within the same dimer row) silicon surface dimers.

10:20am **SS2-MoM7 Carbonyl Chemistry at the (100)-2x1 Semiconductor Interface**, ***M.A. Filler**, S.F. Bent,* Stanford University

Several recent studies of the covalent attachment of organic molecules at group-IV (100)-2x1 semiconductor interfaces reveal that even for simple compounds, complex bonding geometries that may involve multiple surface dimers are probable. In an attempt to gain further insight into the fundamental thermodynamics and kinetics of intra- and interdimer bonding pathways, we have studied the reactions of acetone and acetaldehyde on Si(100)-2x1 and Ge(100)-2x1 using a combination of infrared and X-ray photoelectron spectroscopy. For the Ge(100)-2x1 surface, infrared data of both acetone and acetaldehyde reveal a low coverage peak near 1510 cm@super -1@. Isotopically-labeled derivatives of these compounds provide evidence that this mode corresponds to an interdimer adsorption product where a carbonyl moiety donates charge to a neighboring dimer atom. Additional absorption peaks are observed near 1675 cm@super -1@ for moderate surface coverages and at 1600 cm@super -1@ near saturation, likely resulting from @nu@(C=O) and @nu@(C=C) stretching modes, respectively. These data suggest that, in addition to the previously reported ene product, carbonyl-containing compounds can react to form a C-H dissociation product where the carbonyl moiety remains intact. Results will be discussed within the context of classical organic chemistry, mainly keto-enol tautomerization, acidity, and hydrate formation.

10:40am **SS2-MoM8 Adsorption of Chiral Enantiomers of 2,3 butanediol on Si(100)**, *J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; M. Carbone,* Universita Tor Vergata, Italy*; M. Tallarida, J.H. Dil, **K. Horn**,* Fritz-Haber-Institute der MPG, Germany*; M.P. Casaletto,* Instituto per lo Studio die Materiali Nanostrutturati ISMN, Italy*; R. Flammini,* Istituto de Metodologie Inorganiche e dei Plasmi CNR, Italy*; M.N. Piancastelli,* Universita Tor Vergata, Italy

The adsorption of the chiral L,L- and R,R as well as the achiral R,L enantiomer of 2,3-butanediol on a Si(1 0 0) surface has been investigated by photoelectron spectroscopy. The valence band spectra show features assigned to molecular orbitals of 2,3-butanediol by comparison with calculations, and the surface states of clean Si are removed. The Si 2p reveals core-level shifts with two new components at 0.24 and 0.97 eV from the bulk, which are assigned to Si-H and Si-O bonds, respectively. The C 1s core-level spectrum consists of two major peaks separated by 1.3 eV, which are attributed to carbon atoms in -CHOH and -CH3 groups, in the molecule respectively. From the analysis of the valence band, the Si 2p, C 1s, and O 1s core-level spectra, we conclude that the 2,3-butanediol molecule undergoes a cleavage of the O-H bonds, and is bonded to the surface by the oxygen atoms. The molecule shows no further fragmentation and probably forms a six-membered ring of the O-C-C-O segment with the Si dimer atoms. By using circularly polarized x-rays we were able to observe a sizeable circular dichroism in the C1s core level emission from the different enantiomers. We discuss this finding in its potential to identify the presence of chiral centers in adsorbed molecules.

11:00am **SS2-MoM9 Self Assembly on Si(114)-(2x1): Molecular Attachment Via Alkene Functional Groups**, ***D.E. Barlow**, A.R. Laracuente, L.A. Baker, L.J. Whitman, J.N. Russell, Jr.,* Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5@degree@ between (001) and (111). Because the equilibrium surface reconstruction consists of a single domain of oriented, periodic rows of dimers, rebonded (001) steps, and non-rebonded steps, it is an ideal substrate for examining whether structure-specific reactivity can be used to create organic 1-D nanostructures on Si. We used STM and FTIR spectroscopy to study ethylene and cyclopentene chemisorption on Si(114)-(2x1) in ultra-high vacuum and to characterize the resulting degree of order at the organic-Si interface. Specifically, we examined the orientation, structure, and bonding arrangements of the adsorbates at the various sites on the Si(114) surface. STM and LEED show that well-ordered monolayers can be formed even on this heterogeneous surface. STM images show that the initial adsorption occurs preferentially along a single structural row, rather than by random occupation of multiple binding sites. Polarized transmission FTIR results are consistent with chemisorption of both ethylene and cyclopentene on Si(114)-(2x1) via [2+2] cycloaddition with preferential adsorbate orientation along the rows on the surface. The results clearly demonstrate that Si(114)-(2x1) is a suitable high index surface for organic self assembly using alkene cycloaddition chemistry.

11:20am **SS2-MoM10 Adsorption of Cata-condensed Aromatic Compounds on Si(100)***, K. Okamura, Y. Hosoi, Y. Kimura, H. Ishii,* ***M. Niwano,*** Tohoku University, Japan

We have investigated the adsorption of cata-condensed aromatic compounds on a Si(100)-2x1 surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR). Si samples (prisms) used for MIR-IRAS measurements were prepared from n-type Si wafers and pre-cleaned by the conventional RCA treatment. The 2x1 reconstructed surface was obtained by flashing the sample surface at about 1300 @super o@C following thermal annealing at 900 @super o@C in an UHV chamber. To dose the 2x1 surface with small aromatic compounds (benzene, naphthalene and anthracene), we introduced them into the chamber in gas phase, while larger aromatic compounds were adsorbed on the surface by vacuum evaporation. We have collected IRAS spectra of those aromatic compounds adsorbed on the 2x1 surface, and analyzed the spectra in the region of C-H stretching vibration modes. It is well known that carbon in the sp2 coordinate exhibits absorption peaks in the region of 3000-3100 cm@super -1@, and carbon in the sp3 coordinate shows peaks in the region of 2900-3000 cm@super -1@. All of the measured spectra exhibited C-H stretching vibration peaks at both regions, indicating that some of the carbon atoms of the molecule are transformed from the sp@super 2@ to sp@super 3@ coordinate to form Si-C bonds when the aromatic compounds adsorb on the surface. We observed that these aromatics adsorb on the surface in different manners depending on the surface coverage. Compared with cluster calculation based on the density functional theory method, we determined that small aromatic compounds adsorb in a relatively simple conformation at low coverage, while high-coverage produces some complicated adsorption configurations. Larger aromatic compounds exhibited two different kinds of peaks; one is due to the molecule adsorbed directly on the Si surface (chemisrption), and the other is due to that adsorbed on the monolayer-covered surface (physisorption).

11:40am **SS2-MoM11 Ideal Methyl Termination of the Si(111) Surface***,* ***T. Yamada****, M. Kawai,* RIKEN, Japan*; A. Wawro,* Polish Academy of Sciences, Poland*; S. Suto, A. Kasuya,* Tohoku University, Japan

Si(111) surface ideally terminated by methyl (CH@sub 3@-) groups with a (1x1) periodicity was realized by Grignard reaction of Cl:Si(111)-(1x1). STM discerned a well-ordered (1x1) adlattice covering the Si(111) monoatomic step/terrace features as well as 3-fold-symmetric internal structure of protrusions corresponding to the CH@sub 3@ adsorbates. Reservation of all CH@sub 3@ internal bonds and formation of C-Si bond were confirmed by HREELS.@footnote 1@ Scanning tunneling spectroscopy (STS) exhibited diode-like I-V characteristics involving a new surface-originated occupied density of state at -1.6 eV. This unique electronic structure seems to be reflected on the electrochemical behavior in aqueous solutions. Measurement of vibrational decay time by laser sum-frequency generation is now in process for the internal modes. This finding of (1x1) adstructure led us to consider about the conditions of 2-dimensional ordering of organic moieties. Due to the C-Si covalent bonding, the adsorbates can hardly be mobile and self-assembling by inter-adsorbate interaction cannot be expected. Ordering should basically be originated by one-by-one termination of surface Si, and the adspecies should be accommodated within a hexagonal (1x1) unit cell of Si(111).@footnote 2@ We plan to deposit small moieties, such as CH:::C-, N:::C- and CF@sub 3@- by novel organic reagents. We also critically consider about deposition of long-chain alkyl adsorbates usually studied for purposes of application. The anchoring part of a long alkyl moiety sticks out of the (111) unit cell, and some of the neighborhood Si atoms should be terminated by small adsorbates (such as H and fragmented hydrocarbons). We attempted to approach this problem by investigating the surfaces formed by Grignard reaction with linear-chain alkyl groups (C4 and less). @FootnoteText@ @footnote 1@ T. Yamada et al., J. Am. Chem. Soc. 125 (2003) 8039.@footnote 2@ P. Allongue et al., J. Electroanal. Chem. 550 (2003) 161.

Surface Science
Room 210B - Session SS1-MoA
Simulation and Theory of Adsorption

Moderator: S.B. Sinnott, University of Florida

2:00pm **SS1-MoA1 Theoretical Insights into Chemistry and Catalysis at the Aqueous Metal Interface***, **M. Neurock**,* University of Virginia **INVITED**

The metal-solution interface is important in controlling a number of relevant processes including catalysis, electrocatalysis, and corrosion chemistry. Relatively little, however, is known about the structure and dynamics of the metal solution interface and its impact on elementary physicochemical surface processes, including adsorption, diffusion, and reaction. Density functional theory and ab initio molecular dynamic methods have been used to analyze the effects of aqueous media on the mechanism and the kinetics of different surface processes. The presence of protic solutions on well-defined metal substrates leads to a wealth of interesting surface behavior. Hydrogen bonding can modify the structure of adsorbed intermediates, alter the strength of the adsorbate surface-bond, stabilize charged intermediates, enhance surface kinetics and even provide new mechanistic pathways in which the solution directly participates. We describe the direct, as well as the indirect, effects of solution on different surface processes including the heterolytic dissolution of organic and inorganic intermediates, molecular and dissociative adsorption and desorption of organic intermediates over well-defined metal surfaces, surface reactivity, and diffusion. There are many cases where the solution can directly participate in these mechanisms by directly participating in proton transfer processes. These effects can be quite different in electrochemical systems since the chemical potential can have an important influence on the structure and reactivity at the metal solution interface. We examine here the energetics and pathways for methanol oxidation well-defined Pt(111) substrates over a range of different applied potentials for application to the direct methanol fuel cell.

2:40pm **SS1-MoA3 Atomistic Modeling of CO Oxidation on Pd(100): Ordering of the Reactant Adlayer, Bistability of Steady States, and TPR***, **D.-J. Liu**, J.W. Evans,* Iowa State University

We develop a realistic atomistic lattice-gas model for CO-oxidation on Pd(100) under UHV conditions which describes equilibrium c(2@sq@2 x @sq@2)R45° ordering of CO(ads) on bridge sites, and both non-equilibrium c(2 x 2) and equilibrium p(2 x 2) ordering of O(ads) on four-fold hollow sites. The latter requires suitable treatment of the dissociative adsorption kinetics of O@sub 2@(gas) via an 8-site rule (reflecting strong repulsions between neighboring O) together with transient mobility. CO-CO and O-O adspecies interactions are tuned to match experimental LEED, TPD, and heat of adsorption data for the separate adspecies. Description of the interaction and reaction between CO(ads) and O(ads) is guided by DFT results and by comparison with TPR data. With this model, we map out the bifurcation diagram for the reactive steady states identifying the bistability regime and critical (cusp) point. We also relate various features of the experimental TPR spectra to details of the adspecies interactions in this system. We also discuss extension of the model to the regime of higher pressures, where oxide formation produces a clear signature in the TPD spectra for oxygen, and impacts the reaction kinetics.

3:00pm **SS1-MoA4 CO Coupling Reaction on UO@sub2@(111)Single Crystal Surface: An Experimental and Theoretical Study***, H. Idriss, **S.D. Senanayake**, A.S.L. Soon,* The University of Auckland, New Zealand

The unique electronic properties of UO@sub2@ makes it an ideal prototype material for investigation of new chemical pathways. Carbon monoxide molecules were found to selectively couple to C2 compounds over O-defected surfaces of UO@sub2@(111) single crystal. The most plausible reaction can be described by: 4CO + H@sub2@ -> C@sub2@H@sub2@ + 2CO@sub2@. This unique reaction is studied using temperature programmed desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and valence band, targeting surface intermediates and oxidation states of uranium and oxygen ions. Evidence of CO dissociation upon adsorption is seen by the disappearance of XPS lines due to U metal, the increase of those related to U@super4+@ and the formation of surface carbides. Preliminary steady state catalytic experiments on polycrystalline H@sub2@-reduced UO@sub2@ have further confirmed the selective pathway to acetylene and ethylene. Relativistic density functional theory (DFT) calculations have been performed using the Amsterdam Density Functional Theory for molecules and with BAND code for embedded clusters and periodic slab studies. Binding energies and conformations of CO adsorption on the surface are probed to offer a deeper understanding of surface energetics. The structures of interests were fully optimised with the inclusion of scalar relativistic effects, which were treated with the Zeroth-Order Regular Approximation (ZORA) formalism.

3:20pm **SS1-MoA5 Towards an Understanding of the Silver Catalysed Ethylene Epoxidation Process***, **A. Michaelides**,* University of Cambridge, United Kingdom*; K. Reuter, M. Scheffler,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany

A number of recent studies indicate that, under moderate pressures of oxygen, some transition metal catalysts are covered in thin oxide overlayers. For oxidation catalysis, it has been suggested that such "surface-oxide" layers are catalytically active, and that this role is not performed by the pure metal surfaces as was traditionally assumed. This contemporary picture can be traced back to Ag catalysis, where it has been believed for 30 years that exposure of oxygen to Ag{111} leads to the formation of an ultra-thin surface-oxide. Extensive experimental and theoretical work has been carried out for oxygen on Ag, motivated mainly by the desire to understand silver's unique ability as a partial oxidation catalyst for ethylene [see, for eg., refs. 1-4]. However, density functional theory results, presented here, augmented with thermodynamic calculations, indicate that previous conclusions are significantly incomplete and that the structure of this original surface-oxide must be reconsidered. Indeed novel oxide overlayers are identified, and, predicted to be stable under the oxygen pressures at which the industrial ethylene epoxidation reaction is carried out. Moreover, we find that under these conditions finite variations in the stoichiometry of the surface oxides can occur with practically no change in free energy. It is suggested that this is one of the essential hallmarks of an effective red-ox catalyst. The first phase diagrams of Ag in contact with gaseous environments of both oxygen and ethylene are also be presented, as are reaction mechanisms for the formation of ethylene-epoxide. @FootnoteText@ @footnote 1@C.T. Campbell, J. Catal. 94, 436 (1985). @footnote 2@C.I. Carlisle, M.-L. Bocquet, J. Cerda, D.A. King, P. Sautet, Phys. Rev. Lett. 84, 3899 (2000). @footnote 3@A. Michaelides, M.-L. Bocquet, P. Sautet, A. Alavi, D.A. King. Chem. Phys. Lett. 367, 344 (2002). @footnote 4@W.X. Li, C. Stampfl, M. Scheffler, Phys. Rev. B 68, 165412 (2003).

3:40pm **SS1-MoA6 Determination of Adsorption Site for Isocyanides and Aminocarbynes on Pt(111) from Theoretical and Experimental Vibrational Spectra***, **E. Herceg**, B. Chatterjee, M. Trenary,* University of Illinois at Chicago

Density funcional theory (DFT) calculations have been used to study the bonding, geometry, and influence of basis set size on the vibrational properties of methyl-isocyanide (CH@sub 3@NC) and aminocarbyne species (CNH@sub 2@ and CNHCH@sub 3@) bonded to different Pt clusters. Calculated spectra were compared with the RAIRS data obtained for the corresponding species adsorbed on the Pt(111) surface. We used Pt, Pt@sub 7@H@sub 6@, Pt@sub 2@, Pt@sub 9@H@sub 14@, and Pt@sub 4@ clusters in order to provide models for adsorption at on-top, two-fold bridge, and three-fold hollow sites. Comparison between experimental and calculated spectra showed that CH@sub 3@NC is bonded to the surface at on-top site for low coverages and at both on-top and bridge sites for high coverages. For aminocarbynes bonded to Pt@sub 2@ and Pt@sub 9@H@sub 14@ (models of the twofold bridge site) calculations successfully reproduce experimental spectra. No significant improvement was achieved by using the Pt@sub 9@H@sub 14@ cluster compared with the Pt@sub 2@ model. On the other hand better agreement between experimental and simulated spectra of CH@sub 3@NC and CNH@sub 2@ can be achieved by increasing the size of the basis sets used for both the adsorbate and Pt cluster atoms.

4:00pm **SS1-MoA7 Ab Initio Molecular Dynamics Study of Methanol Adsorption and Reaction on Copper Clusters***, **W.-D. Hsu**, S.B. Sinnott,* University of Florida

The reaction of methanol molecules with size-selected Cu@sub n@ clusters, n=2-9, is investigated by first-principles molecular dynamics simulations. The simulations use density functional theory within the generalized gradient approximation and ultrasoft pseudopotentials. The molecules are deposited on the Cu clusters with an incident energy of 0.5 eV/molecule. The structure, dynamics, and reaction energy are studied as a function of the cluster size. Experiments by Kondow and co-workers@footnote 1@ find that the dominant reactions are methanol chemisorption, demethanation, and carbide formation, which are very different from the interaction of methanol with bare copper surfaces, where physisorption is the dominant outcome. The simulations detail the atomic scale mechanisms that are responsible for these differing behaviors. For example, they show that the adsorption energy of methanol to Cu@sub 7@ is about 0.5 eV, which is larger than the energy of adsorption of methanol on the Cu(111) surface@footnote 2@@super ,@@footnote 3@ by about 0.25 eV. The simulations also illustrate the differences in the interaction of methanol with copper clusters of various sizes. This work is supported by the National Science Foundation (CHE-0200838). @FootnoteText@ @footnote 1@M. Ichihashi, T. Hanmura, R. T. Yadav, and T. Kondow, J. Phys. Chem. A 104 (2000) 11885@footnote 2@J. R. B. Gomes, and J. A. N. F. Gomes, Surf. Sci. 471 (2001) 59@footnote 3@J. Greeley, and M. Marvrikakis, J. Cataly. 208 (2002) 291.

4:40pm **SS1-MoA9 Furan Decomposition Mechanism on Vicinal Pd(111) Studied by STM and DFT@footnote 1@***, A. Loui, C.Y. Fong, S. Chiang,* University of California, Davis

We have used scanning tunneling microscopy to investigate the behavior of furan (C@sub 4@H@sub 4@O) adsorbed intactly on stepped Pd(111) at 199 and 225 K, as well as aspects of its decomposition after heating to a maximum temperature of 415 K. Studies conducted on two substrates with relatively narrow and wide terraces reveal strikingly different behaviors. Furan is shown to preferentially adsorb at step edge sites on both surfaces, while evidence of molecular diffusion is seen only on the narrower vicinal planes. After heating to 288 K, 300 K, and 415 K, evidence of reaction can be observed in occupied-states STM images. Our observations support a furan decomposition mechanism wherein the heterocycle preferentially adsorbs and reacts at upper step edge sites. Although our data do not provide a complete picture of the surface reaction, the proposed model is consistent with previous studies of surface adsorption, diffusion, and reaction on vicinal, low-Miller-index transition metal surfaces. Ab initio calculations based on Hohenberg-Kohn density functional theory (DFT) have been performed for several high-symmetry adsorption modes of furan on flat Pd(111). These results, optimized with respect to planewave basis size and k-point sampling of the Brillouin zone, show that a two-fold chemisorption site is energetically preferred over the three-fold hollow and on-top sites. @FootnoteText@ @footnote 1@ Funded by NSF CHE-0111671.

Surface Science

Room 210C - Session SS2-MoA

Assembled Monolayers

Moderator: M.R. Linford, Brigham Young University

2:00pm **SS2-MoA1 Surface Liquid Behavior of Organic Molecules in Nanoscale Direct Deposition Processes***, **N. Cho**, S. Hong,* Seoul National University, South Korea

Nanoscale direct deposition processes such as dip-pen lithography (DPN) have been extensively utilized to pattern organic molecules on solid surfaces. However, complicated 2-dimensional nanoscale diffusion phenomenon in the DPN process has not been clearly understood yet. We propose the surface liquid-based diffusion model that can fully explain complex humidity and temperature dependence of dip-pen lithography. In addition, the study of the long term dependence of DPN deposition rate and phase-separation in the mixed molecular system revealed strong intermolecular interactions during the DPN diffusion process, which also confirms our surface liquid model.

2:20pm **SS2-MoA2 The First Demonstration of the Gas Phase Modification of Scribed Silicon***, **M.V. Lee**,* Brigham Young University*; S.M. Casey,* University of Nevada, Reno*; M.R. Linford,* Brigham Young University

Chemomechanical Surface Functionalization (CMSF) is a simple and versatile method for patterning and functionalizing silicon surfaces. Using this method very small (ca. 30 nm) features have been scribed on silicon using an AFM, as well as much larger features (many microns) using a diamond tip. To date, CMSF has been demonstrated with a variety of neat liquids, including different alkenes, alkynes, alkyl halides, alcohols, aldehydes, and epoxides. However, in spite of the power of this approach for the direct modification of silicon at any desired point on its surface, a drawback of this method is that the unreacted liquid must be removed from the surface by washing following CMSF. Washing creates an opportunity for unwanted surface reactions and/or surface contamination. A CMSF method that would eliminate the surface cleaning step would be an important advance for this technique. Here we show that that two gas phase reagents (ethylene and acetylene) react with scribed silicon. It is noteworthy that this process takes place in an open laboratory using a simple laboratory apparatus that directs a jet of these reactive gases onto the silicon surface during scribing. The resulting surfaces were characterized by X-ray photoelectron spectroscopy, wetting, time-of-flight secondary ion mass spectrometry, Auger electron spectroscopy, and temperature programmed desorption. @FootnoteText@ Niederhauser, T.L.; Lua, Y.-Y.; Jiang, G.; Davis, S.D.; Matheson, R.; Hess, D.A.; Mowat, I.A.; Linford, M.R. Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces. Angew. Chem. Int. Ed. 2002, 41(13), 2353-2356.

2:40pm **SS2-MoA3 Displacement Printing of Adamantanethiolate Self-Assembled Monolayers***, **A.A. Dameron**, R.K. Smith, J.R. Hampton, P.S. Weiss,* The Pennsylvania State University

We have fabricated 1-adamantanethiolate self assembled monolayers (SAMs) on Au{111} and characterized them with scanning tunneling microscopy (STM). The adamantanethiolate SAMs are highly ordered and have less prominent domain boundaries than alkanethiolate SAMs, but the adamantanethiolate molecules are easily displaced by other molecules both during and after SAM formation. Taking advantage of this displacement, we have used adamantanthiolate SAMs in conjunction with microcontact printing to pattern molecules that are difficult to microcontact print by normal methods. Using STM and lateral force microscopy (LFM) we have studied the molecular order of the printed features.

3:20pm **SS2-MoA5 Controlling Surface Architecture on the sub-100 nm Length Scale with Dip-Pen Nanolithography***, C.A. Mirkin, **K. Salaita**,* Northwestern University **INVITED**

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:00pm **SS2-MoA7 Competition as Design Concept in Self-Assembled Monolayers***, **P. Cyganik**, M. Buck,* St Andrews University, UK

Self-assembled monolayers (SAMs) of aromatic thiols adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM). Our experiments show that a molecular design, which is not based on the usual concept of energy minimization but employs competing forces, opens an unexpected additional dimension in the control of structure and properties of thiol SAMs. Based on thiols which are characterized by a combination of a biphenyl unit and an alkane spacer (CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5, 6), the length of the spacer is chosen such that different factors which determine the energetics of a SAM structure (e.g. sulfur bonding geometry vs. intermolecular interactions) enter in a competing rather than a cooperative way. The SAMs prepared according to this concept show thermally induced irreversible transitions into new structures. This transition is paralleled by striking improvement in the structural perfection of the SAM and changes in the stability against exchange by other thiols.

4:20pm **SS2-MoA8 Tuning of Orientation and Chiral Recognition of a Single Chiral Molecule in Self-Assembly through Modulation of Anchoring Sites***, **B.I. Kim**,* Boise State University*; C.Z. Cai, S.S. Perry,* University of Houston

Rod-like aromatic systems with conducting @pi@-backbones are of interest as potential building blocks for electronic devices. Hydrogen bonding could be used as a conductive linkage of molecular wire on a surface. When we build up a self-assembly with rod-like molecules on a surface through hydrogen bonding, we can use chirality to control the configuration of the nanostructure. Recent studies show that chirality plays an important role in site-specific adsorption of molecules, formation of extended chiral domains, and enhancement of stability of clusters and chains. However, those observations have been limited to specific chiral adsorption configurations without addressing more tunable modification of them for a novel nano-engineering. Here we present scanning tunneling microscopy studies of a chiral molecule with two functionalized benzene rings, 4-trans-2-(pyrid-4-yl-vynyl) benzoic acid(PVBA), on surfaces. PVBA shows chiral separation on Ag(111) but not on Pd(111) while it shows orientational separation on Pd(111) but not on Ag(111). An angle dependent model calculation indicates that the orientation and chiral recognition could be tuned through modulation of double anchoring sites, applicable for flexible nano-wire and chiral separation on the surface.

4:40pm **SS2-MoA9 Resonance-Assisted Hydrogen Bonds Stabilize Guanine Quartet Networks on Solid Surfaces***, **R. Otero**, M. Schöck, L.M. Molina, E. Laegsgaard, I. Stensgaard, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

Hydrogen bonding between DNA bases is one of the main interactions that control the conformation and hence the biochemical function of nucleic acid molecules@footnote 1,2@. Apart from the Watson-Crick model for base pairing@footnote 1@, DNA bases can form other hydrogen-bonded complexes that lead to different DNA structures, like G-quadruplexes@footnote 3@ or i-motifs@footnote 4@. In spite of the increasing evidence for the existence and in vivo function of these DNA structures@footnote 5@, a convincing biophysical model for their stability is still missing. By combining high-resolution, variable-temperature Scanning Tunneling Microscopy (STM) and state-of-the-art Density Functional Theory (DFT), here we show that the DNA base guanine (G) deposited under ultra-clean conditions onto a suitably inert substrate such as Au(111) self-assembles into a hydrogen-bonded network of G-quartets, whose structure corresponds perfectly with the quartet structure of telomeric DNA@footnote 3@ determined by X-ray crystallography. The strong preference of G molecules to form quartets can be explained by a cooperative effect that strengthens the hydrogen bonds within the G-quartet network over the hydrogen bonds in isolated dimers. This result underlines the necessity of going beyond the picture of isolated hydrogen bonds in order to properly describe the interactions between biomolecules. @FootnoteText@ @footnote 1@ Watson, J. D. & Crick, F. H. C. A structure for deoxyribose nucleic acid. Nature 171, 737-738 (1953).@footnote 2@ Sinden, R. R. DNA Structure and Function (Academic Press, San Diego, 1994).@footnote 3@ Sundquist, W. I. & Klug, A. Telomeric DNA dimerizes by formation of guanine tetrads between hairpin loops. Nature 342, 825-829 (1989).@footnote 4@ Gehring, K., Leroy, J.-L. & Guéron, M. A tetrameric DNA structure with protonated cytosine-cytosine base pairs. Nature 363, 561-565 (1993).@footnote 5@ Kipling, D. The telomere (Oxford University Press, Oxford, 2002).

Surface Science
Room Exhibit Hall B - Session SS-MoP
Poster Session

**SS-MoP1 Studies of Hydrogen on Pd{111} at 4 K Utilizing Scanning Tunneling Microscopy and Spectroscopy*, L.C. Fernández-Torres,* *E.C.H. Sykes, P. Han, S.U. Nanayakkara, P.S. Weiss,* The Pennsylvania State University

The interaction of hydrogen with Pd{111} has been investigated with low temperature scanning tunneling microscopy and spectroscopy. Palladium is unique in its ability to both adsorb and absorb hydrogen. Adsorption of low exposures of hydrogen has allowed for the observation of tip-induced hydrogen atom diffusion at 4 K. The diffusion of atomic hydrogen at 4 K has been ascribed to inelastic tunneling of electrons; inelastic electron tunneling spectroscopy (IETS) corroborates this assignment, and the hydrogen atom diffusion barrier has been determined. Adsorption of high exposures of hydrogen results in formation of two ordered overlayer structures: (1x1)-H and (@sr@3x@sr@3)-2H. Absorption of hydrogen into subsurface sites in Pd, concurrent with H diffusion from the bulk, have been attributed as the predominant reasons for two observed phenomena: tip-induced vacancy ordering, and Pd{111} lattice distortion.

SS-MoP2 Quartz Crystal Microbalance and Quadruple Mass Spectrometry Studies of Surface Reactions of @beta@-diketonate Precursors and O Radicals*, T.T. Van,* *J.P. Chang,* University of California, Los Angeles

Pure and Er-doped Y@sub 2@O@sub 3@ thin films are of interest for next generation of microelectronic and optoelectronic devices. In this work, a radical-enhanced atomic layer deposition (ALD) process was developed for synthesizing these materials. Specifically, quartz crystal microbalance (QCM) and quadruple mass spectrometry (QMS) were used to study the surface reaction kinetics of @beta@-diketonate precursors with O radicals. The @beta@-diketonate complexes chosen for this study are Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) M(III), or M(TMHD)@sub 3@, where M = Y or Er. The temperature-controlled QCM was used to measure the real time mass changes, since each reaction steps in ALD cycles causes a specific mass increase or decrease. The evolution of surface species during the deposition was identified and analyzed by QMS. Similar adsorption and desorption kinetics were observed for both Y(TMHD)@sub 3@ and Er(TMHD)@sub 3@. The surface coverage increased with increasing substrate temperature then saturated. The adsorption isotherms were fitted with the simple Langmuir model and the adsorption rate coefficients were found to decrease with increasing temperature. Conversely, the desorption rate coefficients increased with increasing temperature. The apparent activation energies are ~0.25 eV. The desorption of volatile by-products during the O radical pulse resulted in a rapid mass decrease followed by saturation. The critical O radical dose needed to reach this saturation increased with increasing coverage and approached 2 minutes at high coverage. The O radicals, besides effectively remove the @beta@-diketonate ligands, were found to create reactive site for precursor adsorption. Specifically, the mass increase during a subsequent precursor pulse depended linearly on the preceding O radical pulse time. Finally, well-controlled atomic layer deposition of Er@sub 2@O@sub 3@ and Y@sub 2@O@sub 3@ was demonstrated.

SS-MoP4 Chemical Bonding of Saturated Hydrocarbons to Metal Surfaces*, H. Öström,* Stockholm University, Sweden*; L. Triguero,* KTH syd, Sweden*; M. Nyberg,* Stockholm University, Sweden*; H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; L.G.M. Pettersson, A. Nilsson,* Stockholm University, Sweden

We have investigated the electronic and geometric structure of saturated hydrocarbons adsorbed on metal surfaces using x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) in combination with density functional theory (DFT) spectrum calculations. XES, which probes the occupied density of states, reveals new adsorption-induced states, which we assign to interaction between the both occupied and unoccupied CH orbitals and the metal d-band. By performing a systematic investigation of how the XA and XE spectra are influenced by different structural parameters, we conclude that the geometry is significantly distorted relative to the gas phase. The bonding to the surface leads to strengthening of CC bonds and weakening of CH bonds. Comparison between different metals shows that the position of the metal d-band is important for the bonding to the surface. These results can be useful for the understanding of the CH bond cleaving mechanism, which is important in catalysis.

SS-MoP5 UHV Study of Cyclohexane on Zr(0001)*, N. Stojilovic,* *J.C. Tokash, R.D. Ramsier,* The University of Akron

We investigate the behavior of cyclohexane on Zr(0001) with temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) methods. Following 150 K adsorption cyclohexane dissociates at low exposures with no thermal desorption detected. Relatively broad desorption features (400-750 K) of the parent molecules are observed for higher exposures. The TPD profiles change with exposure, and the yields increase monotonically. AES reveals more carbon after annealing to 850 K than immediately after adsorption. Additionally, AES data indicate different forms of carbon before and after annealing. This work improves our understanding of the behavior of carbon impurities on Zr(0001), and of the influence of temperature-dependent surface-subsurface diffusion.

SS-MoP6 Study of the Low-Temperature CO+O@sub 2@ Reaction Over Pd and Pt Surfaces*, E. Podgornov,* University of California, Riverside*; A. Matveev, V. Gorodetskii,* Boreskov Institute of Catalysis, Russia*; F. Zaera,* University of California, Riverside

The kinetics of CO oxidation at low temperature has been studied with effusively-collimated molecular beams (MB) and reactive thermal desorption, combined with an isotope-labeling technique. High-resolution electron energy loss spectroscopy (HREELS), field electron microscopy (FEM), and photoelectron microscopy (PEM) have also been applied to determine the roles of subsurface atomic oxygen and surface reconstruction in self-oscillatory phenomena on Pd(111), Pd(110) and Pt(100) single crystals and on Pd and Pt tip surfaces. It was found that high local concentrations of adsorbed CO during the transition from a Pt(100)-hex reconstructed surface to the unreconstructed 1x1 phase apparently prevents oxygen atoms from occupying hollow sites on the surface, and leads to the formation of a weakly-bound adsorbed atomic oxygen. It was inferred from MB experiments with oxygen isotope that the weakly-bound atomic oxygen is the active form that reacts with CO to form CO@sub 2@ at T = 140-160 K. In the experiments involving FEM, sharp tips of Pd and Pt were used to perform in situ investigations of dynamic surface processes. It was concluded that non-linear reaction kinetics is not restricted to macroscopic planes, since planes as small as 200 Å in diameter show the same non-linear kinetics as larger flat surfaces; regular waves appear under oscillatory reaction conditions and propagate through adjacent crystal nanoplanes because of an effective coupling between them. Additional results from isotope-labeling MB experiments led to the conclusion that adsorbed weakly-bound atomic oxygen, and not "hot" oxygen adatoms (excited transient states of adsorbed oxygen which may appear due to excess energy after the dissociation of O@sub 2@), is the active form of oxygen that reacts with carbon monoxide at low temperatures.

SS-MoP7 Adsorption and Reaction of Butyl Groups on Pt(111)*, I. Lee,* *F. Zaera,* University of California, Riverside

The adsorption and thermal reaction of 1- and 2-butyl moieties on Pt(111) was investigated by using reflection-absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD). The butyl intermediates were prepared via thermal activation of the C-I bond of 1- and 2-iodobutanes, respectively. Buta-1,2-diyl and buta-2,3-diyl were observed after the first dehydrogenation. The subsequent thermal activation of those butyl groups resulted in a competition between reductive elimination to butane and @beta@-hydride elimination to butene. Coadsorption experiments with hydrogen and deuterium were used to characterize hydrogenation and H-D reactions. It was found that the hydrogenation of 1-butyl to butane is enhanced by predosed hydrogen, while 2-butyl favors the dehydrogenation to butene via @beta@-hydride elimination.

SS-MoP8 Wetting Behavior of Liquids and Polymer Solutions on the Micro-patterned Fluoroalkylsilane Monolayer Surfaces*, A. Takahara,* *M. Morita, J. Fukai, H. Ishizuka,* Kyushu University, Japan

Micropatterned fluoroalkylsilane monolayers were fabricated on a Si-wafer substrate by chemical vapor adsorption (CVA) of fluoroalkyltrialkoxysilane and vacuum ultraviolet (VUV)-ray photodecomposition under photomask with line-pattern. Field-emission scanning electron microscopic (FESEM) and atomic force microscopic(AFM) observations revealed that the micropatterned surface of fluoroalkylsilane and bare Si-wafer corresponding to the line-width of photomask was formed. Dynamic and static contact angle measurement revealed the anisotropy of water contact angles parallel and perpendicular to the line direction. Droplets of solution of polystyrene were deposited on the line-pattern by inkjet process from the orifice with a diameter of 50ï�-m It was revealed that the xylene solution was repelled from the oleophobic fluoroalkylsillane surface and the PS stripe corresponding to the line pattern shape was obtained.

SS-MoP9 Solvent and Chain Length Dependence of the Conformational Order in Self-Assembled Dialkylammonium Monolayers on Mica*, G. Haehner,* University of St Andrews, United Kingdom, UK*; M. Zwahlen,* University of St Andrews, United Kingdom*; W. Caseri,* ETH Zurich, Switzerland

The adsorption of cationic surfactants, for example alkylammonium compounds, can be employed to modify the surface properties of layered silicates, such as micas and clays. This process is of significant importance to many industrial applications, ranging from ore flotation in the mining industry and soil treatment to the pharmaceutical, household, food processing and cosmetics industry. The conformational order in adsorbed monolayer coatings is an important parameter for the reliable use of the layers. Dialkylammonium films on mica substrates prepared via ion exchange in solution can exhibit a high degree of order and orientation, similar to thiol-gold systems. We have studied the quality of such films on mica depending on the solvent and the alkyl chain length. Contact angle measurements, photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) were employed to characterize the adsorbed layer. A remarkable difference in the established conformational order was observed for films prepared from different solvents and with different chain lengths.

SS-MoP10 Single Step Functionalization of Scribed Silicon with Acid Chlorides and Epoxides*, C.A. Pew,* *Y.-Y. Lua, W.J.J. Fillmore, M.R. Linford,* Brigham Young University

A perpetual problem in surface modification and functionalization is that of finding better and more convenient ways for creating reactive functional groups on surfaces. Two reactive functional groups of great importance in surface modification, and in organic chemistry in general, are the epoxide ring and the acid chloride group. Here we report that epoxide- and acid chloride-terminated monolayers on silicon can be prepared in a single step by chemomechanically scribing silicon that is wet with a bifunctional epoxide (1,2,7,8- diepoxyoctane) or an acid chloride (adipoyl chloride). Surface modification takes place in an open laboratory with compounds that have not been degassed. We also describe the amine-reactivity of these monolayers, using X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and wetting to prove surface functionalization. Finally, we show that the amine reactivity in these monolayers can be controlled and improved by making mixed monolayers composed of a shorter-chain monofunctional adsorbate and a longer-chain bifunctional adsorbate.

SS-MoP11 Chemical Functionalisation of High Porosity, Nanostructured Thin Films*, S. Tsoi,* *E. Fok, J.G.C. Veinot, J.C. Sit,* University of Alberta, Canada

In sensing and catalysis applications, controlled interaction of nanostructured materials with the outside environment is essential. Control over both the structure and the surface properties of these nano-materials allows optimisation for a wide range of applications. Using an advanced technique known as glancing angle deposition (GLAD)@footnote 1@, we can grow porous thin films with controlled nanostructure and a high surface area easily accessible from the surrounding environment. These structural properties make GLAD films highly suitable for sensing and catalysis; the surface properties can then be controlled through chemical functionalisation. Siloxane-based self-assembly@footnote 2@ has been demonstrated as an effective means for functionalisation of a wide variety of simple flat and freestanding structures. Our work is the first application of this technique to the complex, porous, three-dimensional nanostructures grown using GLAD. Goniometer measurements on as-deposited films (hydrophilic, 0° advancing aqueous contact angle) and films treated with various trichlorosilanes (R-SiCl@sub 3@) (hydrophobic, ~120° contact angle) support a substantial modification of the hydrophilicity of the GLAD film surfaces. X-ray photoelectron spectroscopy and standard electrochemistry measurements confirm that the siloxane-based self-assembly process effectively penetrates the GLAD film surface, allowing complete functionalisation of the 3D structures and underlying substrate. Of particular importance, varying degrees of hydrophilicity of the GLAD structures can be achieved by further functionalising the tail groups of the assembled molecule. Such flexibility in the self-assembly process allows the surface chemistry of GLAD films to be extensively tailored for specific requirements of a wide range of applications. @FootnoteText@ @footnote 1@ K. Robbie and M.J. Brett, J. Vac. Sci. Technol. A 15 (1997).@footnote 2@ J.E. Malinsky, J.G.C. Veinot, et al., Chem. Mat. 14 (2001).

SS-MoP13 Organic Molecules Self Organization on Metal Surfaces and on Insulator Thin Films*, L. Ramoino,* *M. Von Arx, S. Schintke,* University of Basel, Switzerland*; T.A. Jung,* Paul Scherrer Institute and University of Basel, Switzerland*; H.-J. Güntherodt,* University of Basel, Switzerland

Single molecules on surfaces are promising objects to overcome the limits of current silicon based techniques. Molecular properties like self assembling and preferential adsorption are specially interesting in order to evolve from top-down manufacturing methods to bottom-up techniques. Formation of a wide variety of molecular self organized structures has been achieved on metal and semiconductor surfaces. Much less is known about the adsorption and self organization of organics molecules on insulators. However, decoupling molecules from the conductive substrate and building-up metal-insulator as well as semiconductor-insulator patterns is very interesting in the perspective of molecular electronics. It has been shown as STM and STS are profitable tools to study morphology and electronic structure of ultra-thin insulating structures on booth metallic and semiconductor substrates. In addition, by mean of insulating films it should be possible to tune the molecule sample interaction by varying the thickness of the insulating layer. We are studying the growth of ultra-thin NaCl films on different metal surfaces. STM pictures clearly show the formation of ordered 2D islands between 1 and 3 monolayer thick and with a characteristic square shape. Their size can be reliably controlled in a range between a few and hundreds of nanometers. Self-organization of different organic molecules deposited on the NaCl/metal system, has been studied for various molecule substituents and surface coverages. The possible molecule-surface interactions leading to self-assembled molecular structures on ultra-thin insulators are discussed for the different molecules and coverages in comparison.

SS-MoP14 Low Energy Electron Diffraction Study of Dodecanethiol Self-Assembled Monolayers Grown on Pt(100) and Pt(111) by Vapor Deposition*, T.M. Sweeney,* *P.S. Robbert, C.A. Ventrice, Jr.,* University of New Orleans*; H. Geisler,* Xavier University

One of the most popular substrates for growing self-assembled monolayers (SAMs) is the Au(111) surface. This is primarily due to the fact that it does not oxidize during preparation of the SAMs from solution. However, gold is not compatible with conventional Si-based electronics due to its tendency to diffuse into Si. A more promising candidate for the integration of SAMs with Si-based electronic devices is the use of Pt for the growth of the SAMs. Therefore, we have performed a study of the growth of dodecanethiol SAMs on single-crystal Pt(100) and Pt(111) surfaces by vapor deposition in ultra-high vacuum. The clean Pt(100) surface exhibits a four-domain (5x1) reconstruction. Upon deposition of ~0.1 L of thiol, the (5x1) reconstruction is removed. Doses greater than a few Langmuir result in a weak (1x1) pattern, indicative of the growth of a disordered thiol overlayer on the unreconstructed Pt(100) surface. The clean Pt(111) surface does not exhibit a surface reconstruction. Deposition of ~0.1 L of thiol results in a sharp (2x2) LEED pattern, which indicates that the initial sticking coefficient is near unity and that the thiol molecules most likely have a standing up geometry. As with the Pt(100) surface, doses beyond a few Langmuir result in the formation of a weak (1x1) LEED pattern. In addition, we have initiated a study of the electronic properties of these SAMs using angle-resolved photoelectron spectroscopy. The results of these measurements will also be presented.

SS-MoP16 Thermal Decomposition of Generation 4-Polyamidoamine Dendrimers Films: Decomposition Catalyzed by Dendrimer-Encapsulated Pt Particles*, O. Ozturk*, *T.J. Black, F. Parsons, K. Pizzolato, J.S. Ratliff, C.T. Williams, D.A. Chen,* University of South Carolina

The thermal decomposition of hydroxyl terminated generation-4 polyamidoamine dendrimer (G4 OH) films deposited on Au surfaces has been compared with decomposition of the same dendrimer encapsulating a ~40-atom Pt particle (Pt-G4OH). Infrared spectroscopy studies showed that when the films were heated in air to various temperatures up to 275° C, the disappearance of the amide vibrational modes occurred at lower temperature for the Pt-G4OH film. Dendrimer decomposition was also investigated by thermogravimetric analysis (TGA) in both air and argon atmospheres, and decomposition of the dendrimer films on Au surfaces was studied by temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum conditions. For both G4OH and Pt-G4OH films, heating to 100° C resulted mainly in the desorption of small molecules such as H@sub 2@, H@sub 2@O, CO and

CO@sub 2@. Heating the G4OH films to 200° C induced the desorption of larger dendrimer fragments around 72, 84, 98, 127, 146 and 261 amu. For the Pt-G4OH films, mass fragments above 98 amu were not observed at any temperature, but much larger intensities for H@sub 2@ desorption were detected compared to that for the G4OH film. XPS studies of the G4OH films demonstrated that nearly all of oxygen and nitrogen atoms were removed from the surface after heating to 450° C. For the Pt-G4OH dendrimer films, most of the oxygen was also removed after heating to 450° C, but there was little decrease in the intensities of the carbon and nitrogen signals. All of these results are consistent with the fact that the Pt particles inside the G4OH dendrimer catalyze thermal decomposition, allowing dendrimer decomposition to occur at lower temperatures. However, the Pt particles also catalyze bond scission within the dendrimer fragments so that greater concentrations of atomic carbon and nitrogen remain on the surface after heating the dendrimer films in vacuum.

SS-MoP17 Spontaneous Molecular Row Formation of 9,10-Thiolated Anthracene on Cu(111)*, **K.-Y. Kwon**, X. Lin, G. Pawin, K. Wong, B.V. Rao, L. Bartels,* University of California, Riverside

Self-assembled monolayers (SAMs) have been the subject of intense research for the recent two decades due to the fact that they can be used to dramatically modify the chemical, physical and electronic properties of surfaces. Thiolate-SAMs offers powerful opportunities for fundamental studies of electron transport, single molecule devices, control of surface wettability, etc. It is known that both alkane- and arene-thiols stand close to upright on the surface at high coverage. Here, we report on the adsorption structure of 9,10-(diacetylthio)anthracene on Cu(111) at low temperatures in ultrahigh vacuum using scanning tunneling microscopy (STM). Before deprotection of the acetyl group, the molecules are mobile even at 80K. Upon heating of the sample in excess of 180K, the acetyl protection group is removed from the thiol and desorbs, as ascertained by thermally programmed desorption experiments. After renewed cooling of the sample to 80K, we find spontaneous assembly of extended molecular rows of dithioantracene molecules. Studies of the attachment and disattachment of diffusing molecules to the end of the rows at various cryogenic temperatures indicate a barrier of 14.8KJ/mol for this process. At increased coverages the antracenes form extended island with a rectangular unit cell.

SS-MoP18 Effect of Nitrogen Addition on the Liquid Crystal Alignment from Hydrogenated Amorphous Carbon*, **H.J. Ahn**, K.C. Kim, J.B. Kim, H.K. Baik, C.J. Park, J.Y. Hwang, H.K. Kang, D.S. Seo,* Yonsei University, Korea

In order to control the alignment of nematic liquid crystal (LC), nitrogen addition to the hydrogenated amorphous carbon thin films was investigated. The hydrogenated amorphous carbon layer had been developed the novel inorganic alignment layer for ion beam (IB) irradiation method. The IB method preserved some damage of the alignment layer since it was the non-contact alignment type. However, the low pretilt angle and the weak anchoring force were pointed out the vulnerable points. The alignment layer was deposited by plasma enhanced chemical vapor deposition (PECVD), and the nitrogen addition to the amorphous carbon layer could cause the change of pretilt angle. XPS and the contact angle were measured for analysis of the alignment layer and polarized optical microscope (POM) and pretilt angle measurement instrument were used to estimate the LC cells.

SS-MoP19 The Coadsorption of Mercury and Molecular Icosahedra on Cu(100)*, **C.C. Ilie**, L.G. Rosa, S. Balaz, B. Doudin, P.A. Dowben,* University of Nebraska-Lincoln

Mercury and alkali metal mixtures with molecules have a long history in the study of non-metal to metal transitions. Using photoemission and electron energy loss spectroscopy, we have investigated the changes in the electronic structure of molecularly adsorbed orthocarborane films as a function of Hg co-adsorption. Two scenarios for co-adsorption of Hg and the icosahedral molecule closo-1, 2 dicarbadodecaborane (orthocarborane) are considered. The mercury atoms may form a lattice which weakly interacts with orthocarborane lattice, or Hg may form a layer between the Cu substrate and orthocarborane molecular film. Mercury 5d@sub 5/2@ shallow core level widths in photoemission suggest interaction with the molecular film, but the binding energies of the molecular orbitals induced photoemission feature suggest that the interaction is weak.@FootnoteText@D. N. McIlroy, Jiandi Zhang, P. A. Dowben, P. Xu and D. Heskett, "Surface Science", 328, 47-57 (1995)

SS-MoP21 Reactivity of Metal Carbide Surfaces and Nanoparticles: a Density Functional Study*, **P. Liu**, J.A. Rodriguez, J.T. Muckerman,* Brookhaven National Laboratory

The destruction of S-containing molecules is a very important issue in the chemical industry and the control of environmental pollution. The reactivity of metal carbide surfaces, M@sub2@C(001) (M=Ti,V,Mo) and MC(001), as well as M@sub8@C@sub12@ (metallocarbohedrene, metcar in short) nanoparticles towards sulfur, sulfur dioxide and thiophene was investigated using density functional theory. Our study reveals unexpected ligand and steric effects. Due to the corner or edge sites (ligand effect), the M@sub8@C@sub12@ nanoparticle behaves as active as M@sub2@C(001) towards sulfur and sulfur dioxide in spite of the high C/M ratio and C@sub2@ groups. Spontaneous S-O bond cleavage was observed on both M@sub8@C@sub12@ and M@sub2@C(001). In contrast, these adsorbates bond weakly with MC(001), and there is an activation barrier for the decomposition of SO@sub2@ on MC(001). Contrary to common assumptions, the C atoms are not simple spectators and play a key role in the energetics for the dissociation of sulfur dioxide. In the case of thiophene adsorption, only M@sub2@C(001) exhibits a high reactivity that leads to a spontaneous S-C bond cleavage. The interaction of thiophene with both MC(001) and M@sub8@C@sub12@ is weak. On the nanoparticle, steric repulsion between the C@sub2@ groups and thiophene overcomes the high reactivity of the Mo atoms in corner or edge sites (ligand effect). Our results illustrate the complex interplay of ligand and steric effects in nanoparticles of metal compounds.

SS-MoP22 Adsorption of Hydrogen on CNT Surfaces and Surface Chemistry on HOPG*, **J. Nakamura**, E. Yoo, M. Ishihara, T. Habe, N. Yagai, E. Matsuyama, T. Matsumoto,* University of Tsukuba, Japan

Hydrogen storage by carbon nanotubes, graphite and the other carbon materials have been studied from the viewpoints of chemisorption of hydrogen at atmospheric pressure. We find that deposited Pd nanopraticles and formation of defects produced by oxidation increased the chemisorption of H atoms (2 - 4 wt%) on CNT surfaces. IR spectra showed peaks assigned to CH@sub 2@ . Desorption of hydrogen was observed around 700 K. In order to study the site of hydrogen on carbon surfaces with scanning tunneling microscopy (STM), we used highly oriented pyrolytic graphite (HOPG) surfaces as a model surface. The hydrogen adsorption is not observed on a clean HOPG surface by STM after dosing H2 or atomic H at 300 K. Temperature programmed desorption (TPD) experiment gives no desorption peak and small desorption peak of H@sub 2@ (m/e=2) at ~570 K assignable to H atoms adsorbed at step edges. Defects are produced on HOPG by Ar ion sputtering and annealing at 1173 K. Bright hillocks are observed by STM, and are assigned to pits in graphene sheets due to high local density of states of sp3-like dangling bonds produced by removing adjacent carbon atoms. After dosing atomic H on the defective HOPG at 300 K, the STM topographs show dark lines on the bright hillocks. The average height of the hillock also decreases from 0.71 nm to 0.32 nm. The average height of the hillocks is recovered to 0.69 nm by heating the sample to 873 K where H desorbed fully from the HOPG surface on a TPD spectrum. These results indicate that the atomic H adsorbed on the defect sites at 300 K, and the local density of states was lowered around the pits.

SS-MoP23 An in situ XPS Study of Fresh Hydrogenated Amorphous Carbon Films*, **Y. Yun**, A.J. Gellman,* Carnegie Mellon University

In order to develop vapor phase lubrication of hydrogenated amorphous carbon (a-CHx) films for use in hard disk manufacturing insights are needed into the fundamental surface chemistry of vapor deposited lubricants. In vapor phase lubrication, fresh a-CHx will be exposed to lubricants directly. Unfortunately, our current understanding of lubricant surface chemistry on a-CHx is based on studies performed on air-exposed, oxidized a-CHx films. Magnetron sputtering has been used to deposit films in ultra-high vacuum under varying conditions. These films have been characterized by Raman spectroscopy to show that they have characteristics similar to those used commercially. X-ray photoelectron spectroscopy (XPS) was used to study the oxidation of fresh a-CHx during controlled exposure to O2. The film surface saturated at ~20% oxygen after a 20 hour exposure to O2 at 10-4 Torr. One can estimate that under atmospheric conditions where the partial pressure of O2 is roughly 200 Torr, the a-CHx film will be oxidized in a few milliseconds. Thus oxidation of a-CHx is unavoidable between removal of the media from vacuum and dip-coating with lubricant.

SS-MoP24 Experimental Study of Cluster Size Effects on Damage Formation by Size-selected Gas Cluster Ion Beams*, **N. Toyoda**, I. Yamada,* University of Hyogo, Japan

A size-selected gas cluster ion beam (GCIB) system has been developed to study the size effects of energetic large cluster ion bombardments on a solid surface for the first time. This system equipped a permanent magnet with a magnetic flux density of 1.2 T. There is a sliding detector and sample holder on a guiding rail perpendicular to the incoming cluster beam axis. By locating a sample at a certain position, particular size of cluster ion can be irradiated continuously with affordable ion current density. With this magnetic filter, the cluster size distribution became 1/20 of those obtained in the conventional GCIB systems. Cluster size effects on damage formations in Si substrates were studied with the size-selected cluster ion beams. When the total acceleration energy of Ar-GCIB was 5keV, both amorphous and oxide thickness on Si substrate increased with decreasing cluster size. In the case of cluster size above 10,000, the irradiation damage in Si was dramatically reduced. This result showed good agreement with that obtained from molecular dynamics simulations. It indicated that very low-damage surface processing can be possible by controlling both the acceleration energy and the cluster size.

SS-MoP25 Plasma Base Ion Implantation Sterilization Technique and Ion Energy Estimation*, **S. Watanabe**,* Soken Kogyo Co., Ltd, Japan*; T. Tanaka,* Hiroshima Institute of Technology, Japan*; K. Shibahara, S. Yokoyama,* Hiroshima University, Japan*; T. Takagi,* Hiroshima Institute of Technology, Japan

Plasma base ion implantation (PBII) with negative voltage pulses to the test specimen has been applied to the sterilization process as a technique suitable for three-dimensional work pieces. Pulsed high negative voltage (5µs pulse width, 300 pulses/s, -800 V to -13 kV) was applied to the electrode in this process at a gas pressure of 2.4 Pa of N@sub 2@. We found that the PBII process reduced the numbers of active Bacillus pumilus cell using N@sub 2@ gas self-ignitted plasma generated by only pulsed voltages. The number of bacteria survivors was reduced by 10@super -5@ x with 5 min exposure. As the ion energy is the most important processing parameter, a simple method to estimate the nitrogen ion energy calculated using distribution for nitrogen in Si implanted by PBII was developed. The implanted ion energy is discussed from the SIMS in depth profile.

SS-MoP26 Size-Dependent Resonant Inelastic X-ray Scattering of Ligand-Stabilized Cobalt Nanoparticles in Liquid Suspension*, **H. Liu,*** Lawrence Berkeley National Laboratory*; G. Thornton,* University College London, UK*; J.-H. Guo,* Lawrence Berkeley National Laboratory*; Y.D. Yin,* University of California, Berkeley*; A. Augustsson, C.L. Dong,* Lawrence Berkeley National Laboratory*; A.P. Alivisatos,* University of California, Berkeley*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The electronic properties of cobalt nanoparticles suspended in liquid have been investigated using synchrotron-based resonant inelastic x-ray scattering (RIXS) spectroscopy. Cobalt nanoparticles of 3, 4, 5, 6, and 9 nm were synthesized using wet-chemical methods. Liquid suspensions of the samples were then sealed into a vacuum-compatible cell closed with an x-ray transparent silicon nitride window, which separated the liquid from the surrounding vacuum during measurements. The experiments were carried out at beamline 7.0.1 of the Advanced Light Source (ALS). Particle oxidation was prevented by performing spectroscopy under the conditions of synthesis. RIXS spectra revealed two main features with energy losses of 1.8 eV and 6 eV. The 1.8 eV feature was assigned to excitations from the ground state to a final state dominated by the 3d@super n@ configuration electrons (dd transition), while the 6 eV feature was assigned to charge transfer from the ligand/solvent molecules to metal atoms with a 3d@super n+1@L@super -1@ final state. RIXS spectra excited at the Co 2p@sub 3/2@ XAS peak position showed that the intensity of the 1.8 eV peak (dd excitation) decreased with decreasing particle size. The charge transfer feature also shifted significantly, from ~ 6.9 eV for 9 nm nanoparticles to ~ 6.0 eV for smaller particles. This difference can be attributed to changes in the interaction between the metal core and the ligand/solvent molecules with nanoparticle size.

SS-MoP27 Design of a High-Speed Digital Feedback Loop for Scanning Tunneling Microscope Applications*, **E. Ulin-Avila**, A. Liu, B.V. Rao, L. Bartels,* University of California, Riverside

We present the development of a digital feedback loop for Scanning Tunneling Microscope (STM) operation that is capable of updating the tip height and xy position at a frequency of 170kHz. This feedback frequency approximates the maximum update rate of standard 16bit AD/DA converters of 200kHz. Its digital nature allows for precise linearization of the exponential dependence of the tunneling current on the tip-sample separation thereby avoiding oscillatory behavior common with non-linearized feedback loops. In addition, the digital setup allows full control of the z-motion of the tip at any point in time, which permits versatile tip control during lateral manipulation and rapid spectroscopy. The feedback loop incorporates a commercial digital signal processor board (Innovative Integration) utilizing a TI C6200 processor. First application of the new system will be presented.

SS-MoP28 Potential-induced Surface Stress at the Solid-liquid Interface Measured with a Differential Microcantilever-based Sensor*, **V. Tabard-Cossa**, M. Godin,* McGill University, Canada*; L.Y. Beaulieu,* Memorial University, Canada*; R.B. Lennox, P. Grutter,* McGill University, Canada

We report on a differential microcantilever-based system capable of measuring surface stress changes which occur during electrochemical reactions. Our system is composed of two microcantilever sensors. The first active microcantilever serves as the working electrode (in a conventional three-probe electrochemical cell configuration) and as the mechanical transducer (bending of the microcantilever), yielding simultaneous, real-time, in situ measurements of the current and interfacial stress changes. A second microcantilever serves as a reference sensor to detect any unwanted cantilever deflection resulting from temperature variations, mechanical vibrations and/or uncontrolled chemical reactions. This micromechanical cantilever sensor has a deflection sensitivity of 0.2 nm, which translates to a surface stress sensitivity of 1x10@super -4@ N/m with a dynamic range up to 50 N/m. This system is used to study the potential-induced surface stress at the solid-liquid interface for the case Au in 0.1 M HClO@sub 4@. The dependence of surface stress on surface charge density is examined for different Au surface morphologies. The role played by the morphology of the sensing substrate in microcantilever sensors is studied in order to understand the origin of the surface stress responsible for the sensor's response.

SS-MoP29 Selective Detection of Cr(VI) Using a Microcantilever Electrode Coated with a Self-Assembled Monolayer*, **F. Tian**,* Oak Ridge National Laboratory*; V. Boiadjiev,* University of Tennessee in Knoxville*; L. Pinnaduwage, G. Brown, T. Thundat,* Oak Ridge National Laboratory

We have demonstrated detection of Cr(VI) ions using functionalized cantilevers under electrochemical control. Au-coated microcantilever working electrodes are modified with self-assembled monolayer of 4-mercapto-pyridinium in sulfuric acid solution. Differential surface stress changes at the modified microcantilever have been measured to determine Cr(VI) by monitoring the potential-induced deflection of the microcantilever and simultaneous current-potential response by cyclic voltammetry. In an electrolyte containing sulfuric acid alone, the increase of potential causes a compressive surface stress resulting in the microcantilever bending away from monolayer coated Au side. Stressogram (first derivative of stress with respect to potential vs electrode potential) shows sweep rate independence, which is consistent with voltammetry. In the presence of 10@super -4@ M Cr(VI), a compressive stress peak can be observed during cathodic sweep. Surface stress characteristics continue to change during potential cycling at each fix sweep rate although the measured current-potential responses in the voltamogram are still constant. It suggests that there is a strong adsorption of Cr(VI) on pyridinium monolayer coated microcantilever electrode. Because of the adsorption of Cr(VI), the stressogram behavior is only consistent with voltamogram in the very beginning of sweep cycling and at much higher sweep rates. Our results demonstrate that the observed changes of differential surface stress are due not only to potential change, but also to ion adsorption/desorption and electron exchange at the electrode surface. Such potential controlled microcantilever technique offers new insights into the behavior of the solid-liquid interface during electrochemical reactions at modified electrodes.

SS-MoP30 Formation of Supramolecular Cavitands on Electrode Surfaces*,* *C. Safarowsky, A. Rang, C.A. Schalley, K. Wandelt, **P. Broekmann**,* University of Bonn, Germany

Supramolecular host-guest recognition is one the most challenging topics in modern chemistry and physics as well. Combining supramolecular approaches with state of the art surface science techniques allows to gain new insights about the structure and dynamics of supramolecular assemblies which are adsorbed at surfaces. In this contribution we present two approaches to realize supramolecular architectures at electrode surfaces in an electrochemical environment. The most prominent property of these architectures is their molecular host-cavity in which smaller guest molecules can be incorporated. Our method of choice to investigate these electrochemically fabricated arrays of host assemblies is the in-situ scanning tunnelling microscopy. Our first approach is based on the selforganization of small monomers to supramolecular assemblies at the surface. For this purpose we use redox-active dibenzyl-viologen cations which arrange on a chloride modified Cu(100) surface with the formation of square-shaped host assemblies consisting of 4 individual molecules. Characteristically, these assemblies are chiral and, hence, occur in two mirror-domains on the electrode surface. Our second approach is based on the direct adsorption of pre-assembled supramolecular units at the electrode surface from the solution phase. For this purpose we use so called Fujita-squares which are characterized by a fourfold-symmetric arrangement of 4 Pt(II)-cations stabilized by 4 bipyridine ligands and 4 further ethylenediamine molecules. These cationic molecules can also be adsorbed on a chloride modified Cu(100) electrode surface. In both cases we end up with molecular cavities which are oriented towards the solution phase and can, thus, be directly imaged by in-situ STM. The size of these cavities amounts to 1 nm in both cases.

SS-MoP31 Low Temperature Ultra-High Vacuum Scanning Tunneling/Force Microscopy for Single-Molecule Imaging and Spectroscopy*, **T. Shimizu,*** University of California, Berkeley*; A. mugarza,* Lawrence Berkeley National Laboratory, University of California*; Y. Qi,* University of California, Berkeley*; M. Heyde, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory, University of California

A low temperature ultra-high vacuum scanning tunneling/force microscope (LT UHV STM/SFM) has been designed and constructed for imaging, spectroscopy, and manipulation at the atomic scale. This microscope is capable of operating in either STM or SFM modes through in-situ tip exchange. In addition, simultaneous STM/SFM is also possible using a conductive SFM tip. Our goal is to investigate inter- and intra-molecular forces between small molecules on metal surfaces, to explore the relation between electronic and mechanical properties, and to perform electronic, vibrational, and force spectroscopy. Preliminary STM images and scanning tunneling spectra of single-molecules will be presented.

SS-MoP32 Extracting Single Molecule Statistics from Scanning Probe Images*, **B.A. Mantooth**, E.C.H. Sykes, P. Han, P.S. Weiss,* The Pennsylvania State University

Scanning probe microscopes have enabled the unprecedented real-space visualization of single molecules and atoms on surfaces. Analyses of time-resolved sequences of these images allow the quantification of site-specific interactions and dynamics of adsorbed species. We have used scanning tunneling microscopy to probe and to quantify the weak substrate-mediated interactions in benzene overlayers on Au{111} at 4 K, and to characterize concerted motions of molecular cascades in these benzene overlayers. We use similar techniques to characterize the correlation of CO adsorption site with the charge density waves of the surface state of Ag{111}.

SS-MoP33 Site-selective Electroless Plating on Amino-terminated Diamond Substrate Patterned by 126 nm Vacuum Ultraviolet Light Lithography*, **A. Hozumi,*** National Institute of Advanced Industrial Science and Technology, Japan*; N. Shirahata,* National Institute of Materials Science, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan*; Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology, Japan

The use of diamond substrates to manage heat dissipation in microelectronics has recently attracted considerable attention. Diamond metallization technique is of crucial importance in order to fabricate microelectronics devices. However, due to its excellent chemical inertness, it is hard to fabricate metal circuitry on the diamond substrates. Here we report a spatially defined metallization of copper (Cu) through an electroless plating on the amino-terminated diamond surface micropatterned by vacuum ultraviolet (VUV) photolithography. A diamond surface was first photochemically hydrophilized using VUV light of 126 nm. Due to VUV irradiation, the diamond surface became completely hydrophilic with its water-contact angle changing from 102° to 5° or less. According to X-ray photoelectron spectroscopy, polar-functional groups, such as C-O and C=O/O-C-O, were formed on the surface. Amino-terminated organosilane molecules were then chemisorbed onto the photochemically modified surface through a vapor phase. Next, the sample was exposed to 126 nm VUV light through a mesh mask, and subsequently immersed into a PdCl@sub 2@ solution kept at pH 5 for 30 min and rinsed with Milli-Q water. Finally, the substrate was immediately immersed into a commercial electroless Cu plating bath for 2 min at room temperature. Cu film with about 40 nm thick was site-selectively deposited onto the amino-terminated surface and remained free of deposits in the VUV-irradiated regions, as evidenced by an optical microscopy. The well-defined Cu microstructures were successfully formed on the diamond surface. Due to thermal treatment at 200 °C for 3 h in vacuum, a resistivity of the Cu film decreased from 17.1 µ@ohm@ cm to 13.4 µ@ohm@ cm.

SS-MoP34 Nanotribological Effects of Hair Care Products and Materials on Wet and Dry Human Hair using AFM/IFM*, C. LaTorre,* The Ohio State University*; **B. Bhushan,*** The Ohio Sate University

Tribological properties such as friction have been well studied for hair and other biological materials on the macroscale. Lower macroscale coefficient of friction values have been reported in literature for hair treated with various conditioning agents, as opposed to untreated virgin hair. The mechanisms behind lower friction with the application of conditioning products are understood on the macroscale level. However, the interactions between hair and hair care products that occur on the micro/nano scale and the tribological effects of these interactions are not as well understood. Major sources of investigation for treated hair includes localization of various conditioning products, mechanisms behind changes in friction and adhesion on the nanoscale due to conditioner agents, and how the products change the microstructure of the cuticle. The paper presents nanotribological studies investigating adhesion and friction using AFM/LFM. Test samples include Caucasian, Asian, and African hair at virgin and treated conditions in both wet and dry environments. Friction and adhesion measurements were taken using a Si@sub 3@N@sub 4@ tip and constant force mode in AFM/LFM. Friction force mapping provides insight into the localized change in friction caused by the application of hair care materials. Force-volume plots to study adhesion on the cuticle surface provide information about localization and change as well. A discussion is presented on these properties of hair as a function of ethnicity, wet and dry environments, and conditioning treatments.

SS-MoP35 A New @super 3@He Spin-Echo Spectrometer for Ultra-High Resolution Inelastic and Quasi-Elastic Helium Atom Scattering*, A.P. Jardine,* University of Cambridge, UK, U.K.*; P. Fouquet, S. Dworski, **G. Alexandrowicz**, H. Hedgeland, J. Ellis, A. Allison,* University of Cambridge, UK

Quasi-elastic helium atom scattering (QHAS) is a unique tool for studying surface dynamics on atomic length and picosecond time scales@footnote 1@. Conventional QHAS experiments, using time-of-flight methods, have limited resolution due to the velocity spread in the probing helium beam and can only investigate exceptionally fast processes. The recently established technique of @super 3@He spin-echo@footnote 2@@footnote 3@ is not limited by the velocity spread and can be used to study surface diffusion events over much greater time scales. The method is based on manipulating the precession of the nuclear spin in a polarised beam of @super 3@He atoms. Any energy change at the surface is seen as a change in the final polarisation of the beam. The key difficulty in applying the SE techniques to surface studies is in achieving a fully spin-polarised beam at sufficiently high energy (~8 meV) for a sufficient range of momentum transfers to be probed, to allow full k-space mapping of surface processes. We have have recently completed commissioning of a unique @super 3@He Spin-Echo apparatus, which operates at such beam energies. We show that the instrument increases the range of measurable time scales by three orders of magnitude. The main features of the apparatus are described, and we illustrate its the scope of application with recent experimental data, not only for surface diffusion, but also for the measurement of surface vibrations and helium-surface potentials. The results have unprecedented accuracy. @FootnoteText@ @footnote 1@ A. P. Jardine, J. Ellis and W. Allison, J. Phys. Condens. Matter 14, 6173 (2002)@footnote 2@ M. DeKieviet et. al. Phys. Rev. Lett. 75, 1919 (1995)@footnote 3@ M. DeKieviet et al. Surf. Sci. 377-379, 1112 (1997).

SS-MoP36 Electrochemical Micromachining with Ultrashort Voltage Pulses: Modeling and Simulation*, **J. Kenney**, G.S. Hwang,* The University of Texas at Austin

Recent results using electrochemical systems show promise for the areas of three-dimensional etching, high aspect ratio etching, and controlled deposition. These methods employ a â?otoolâ?⍰ electrode held in close proximity (~1 micron) to a reactive â?osubstrateâ?⍰ electrode in the presence of an electrolyte and utilize ultrashort (~50 ns) voltage pulses to modify the substrate surface selectively. The shape and feature resolution of synthesized structures would be determined by a complex combination of i) charging and discharging of electrochemical double layers at electrode surfaces, ii) electrochemical reactions on the electrodes, and iii) transport of molecules to the electrode surface. Experiments may provide many clues to the fundamental behaviors of electrochemical systems, but their interpretations often remain controversial due largely to difficulties in direct measurement. While current experimental techniques are still limited to providing complementary real space information, the interplay between experiment and theory will contribute to uncovering intricate kinetic phenomena involved in the electrochemical micron-scale patterning. In this talk, we present our multiphysics computational model for electrochemical micromachining with ultrashort voltage pulses. This approach integrates i) a circuit model to describe charging and discharging of electrochemical double layers and electric field variation in electrolytes and ii) the level set method to simulate feature profile evolution during electrochemical etching. Our simulation results of transient current responses and etch profile evolution are qualitatively in excellent agreement with experimental observations. From our simulations, we find that the resolution of etched features is a strong function of the substrate double layer capacity which may be controlled by electrolyte concentration and pulse duration.

SS-MoP37 Measurement of Gibbs Free Energies of Surfaces in Vacuum, and their Use to Explain the Pressure Dependence of the Thickness of a Lead-Oxide Film*, L. Bouzidi,* ***A.J. Slavin,*** Trent University, Canada

A method has been developed, using a high-stability quartz-crystal microbalance (HS-QCM)@footnote 1@, for determining the difference between Gibbs free energies of different surface oxide phases in ultrahigh vacuum. This is the only technique capable of such measurements, to our knowledge. These measurements have been used to explain the dependence, on oxygen pressure, of the thickness of a lead-oxide film grown on a gold substrate. The HS-QCM has also been used to measure a Pb:O ratio of 1:1, suggesting PbO as the surface oxide. Only the surface Pb monolayer oxidizes at an O@sub 2@ pressure of 5 x 10@super -6@ torr, with 1 x 10@super -4@ torr required to oxidize a second layer. For large Pb deposits on Au only the top two layers are oxidized up to an oxygen pressure of 10@super -2@ torr, apparently due to kinetic limitations. These results are quite different from the oxidation of pure Pb. @FootnoteText@ @footnote 1@ L. Bouzidi, S.S. Narine, K.G. Stefanov and A. J. Slavin; Rev. Sci. Instrum. 74, 3039-3044 (2003). .

SS-MoP38 Chemical Binding of N-Containing Aromatic Molecules on Si Surfaces: Mechanistic Understanding of the Selectivity of Reaction Channels*,* ***F. Tao,*** Princeton University*; G.Q. Xu,* National University of Singapore, Singapore

Chemical binding of organic molecules on Si surfaces is an important approach for fabricating molecular architectures to develop Si-based molecular devices and biosensors. Our studies on attachment chemistry of pyrrole, N-methylpyrrole and pyridine demonstrate the diversity of reaction channels of aromatics on Si surfaces. Pyrrole dissociatively chemisorbs onto Si surfaces through breaking the N-H bond, forming a pyrrolyl ring. Due to the absence of the N-H bond, N-methylpyrrole covalently binds to Si surfaces via pericyclic reactions. The difference of chemisorption mechanism between pyrrole and N-methylpyrrole demonstrates a strategy of switching the reaction channel by introducing substituted group. Besides the pericyclic reaction, pyridine can chemically bond to Si surfaces with the formation of SiN dative bond. Compared to pyrrole and N-methylpyrrole, the ability of pyridine to form a dative bond results from higher electron density around the N atom. This is due to localization of the lone-pair electrons on the N-atom for pyridine, contrasted with participation in the aromatic conjugation for pyrrole and N-methylpyrrole.

Surface Science
Room 210B - Session SS1-TuM
Catalytic Reactions: The Role of Surface Steps and Structure
Moderator: G.B. Fisher, Delphi Research Labs

8:20am **SS1-TuM1 Surface Reactions and Catalysis***, **G.A. Somorjai,*** Lawrece Berkeley National Laboratory and University of California, Berkeley **INVITED**

New techniques developed over the past ten years permit the monitoring of surface structure and surface composition at high pressures and at solid-liquid interfaces. Among them sum frequency generation (SFG) vibrational spectroscopy and high pressure scanning tunneling microscopy high pressure (STM) have been used in my laboratory to monitor catalyst surfaces during reaction. C-H bond activation was studied using C6 hydrocarbons, and reaction intermediates that produce branched isomers or benzene on platinum (111) surfaces (both components of high-octane gasoline) were detected by SFG. High pressure STM reveals surface mobility of adsorbates during catalytic hydrogenation and active metal surfaces. Poisoning the reaction by the coadsorption of carbon monoxide also produces ordered surface structures. These studies indicate that diffusional mobility of adsorbates correlates with catalytic activity.

9:00am **SS1-TuM3 The CO-oxidation Reaction on Pt(111) and Pt(553): The Role of Steps***, **J.N. Andersen,** J. Gustafson, M. Borg, A. Mikkelsen, J. Weissenrieder, E. Lundgren,* Lund University, Sweden*; W.X. Li, B. Hammer,* Aarhus University, Denmark

Catalytic materials often consist of small metallic particles dispersed on a support. The large proportion of undercoordinated (edge) atoms on such small particles may substantially influence the catalytic activity. Experimentally, the influence of undercoordinated atoms may be scrutinized by studying vicinal surfaces using methods that allow separate monitoring of what happens at the steps. Theoretically, the effects may be simulated using density functional theory (DFT) based total energy calculations. We present experimental and theoretical results for the adsorption of O and CO as well as for the CO-oxidation on Pt(111) and Pt(553) surfaces using high resolution core level spectroscopy and DFT based slab calculations. The results directly demonstrate that Pt(553) is more efficient in oxidizing CO than Pt(111), and allow us to obtain a very detailed picture of the microscopic processes responsible for this increased reactivity. A crucial result is the experimental and theoretical demonstration that CO molecules adsorbed at steps and on terraces, respectively, can be distinguished via their C 1s binding energies. These C1s fingerprints allow us to follow in a very detailed manner where CO molecules adsorb and react with preadsorbed oxygen. We study the CO oxidation by preadsorbing oxygen at 310K followed either by exposure to CO at the chosen reaction temperature or by annealing at the chosen reaction temperature of a CO overlayer adsorbed at low temperature. The results show that the CO2 production is more efficient on Pt(553) than on Pt(111). By utilizing the mentioned core level fingerprints, we show directly that the increased oxidation rate on Pt(553) is due to that the oxygen adsorbed in the proximity of steps is more reactive than oxygen adsorbed on the terraces. Comparison to theoretical results from DFT proves vital in fully understanding these experimental results and constructing the detailed microscopic model.

9:20am **SS1-TuM4 Controlling the Catalytic Reactivity and Selectivity of Ni Surfaces by Step Blocking**, ***R.T. Vang,*** University of Aarhus, Denmark*; K. Honkala,* Technical University of Denmark*; S. Dahl,* Haldor Topsøe A/S, Denmark*; E.K. Vestergaard, J. Schnadt, E. Lægsgaard,* University of Aarhus, Denmark*; B.S. Clausen,* Haldor Topsøe A/S, Denmark*; J.K. Nørskov,* Technical University of Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Step or defect sites have been shown to dominate the reactivity of catalytic surfaces for the dissociation of a number of diatomic molecules, but so far no studies have addressed the influence of steps in the decomposition of more complex molecules. In most catalytic processes involving hydrocarbon molecules, selectivity (between, e. g., C-H and C-C bond breaking) is crucial for the overall efficiency of the catalyst. In this study we have used STM and DFT calculations to investigate the dissociative adsorption of a simple molecule, CO, as well as a more complex molecule, ethylene (C@sub 2@H@sub 4@), on Ni(111). The STM studies reveal that both molecules decompose at the step edges at a much higher rate than on the (111) facets. These observations are supported by DFT calculations showing a much lower activation barrier for decomposition at a step site compared to a terrace site. Furthermore, the steps are shown to have a crucial influence on the selectivity of the Ni(111) surface towards ethylene decomposition, in the sense that the step effect is much more pronounced for C-C bond breaking than for C-H bond breaking. We also demonstrate how we can control the number of active step sites and thus the reactivity by depositing small amounts of Ag, which from STM studies are shown to block all the step sites on the Ni(111) surface. Finally we exploit this new principle of step control by synthesizing a new high-surface area supported NiAg alloy catalyst. We show in flow reactor tests that the NiAg catalyst has a much lower activity for ethane hydrogenolysis than a similar Ni catalyst, thus confirming that we can block C-C bond breaking by step control.

9:40am **SS1-TuM5 High Pressure Scanning Tunneling Microscopy Study on CO Poisoning of Ethylene Hydrogenation on Metal Single Crystals***, G.A. Somorjai,* University of California, Berkeley*; **D.C. Tang**[1], M. Salmeron,* Lawrence Berkeley National Laboratory*; K.S. Hwang,* University of California, Berkeley

The nature of catalyst poisoning under reaction conditions is an important question in catalysis science@footnote 1@@super ,@@footnote 2@. During a reaction the catalyst surface is covered with a dense layer of adsorbates in equilibrium with the gas phase. This layer consists of reactants, inactive spectator molecules, and active poisoning adsorbates@footnote 3@. For the reaction to occur the surface should remain flexible, atomic rearrangements should be possible, and adsorbate mobility should be high enough so that favorable adsorption sites can be accessed. Using a high pressure scanning tunneling microscope we monitored the co-adsorption of hydrogen, ethylene and carbon dioxide on rhodium (111) and platinum(111) crystal faces in the mTorr pressure range at 300 K in equilibrium with the gas phase. We show that poisoning occurs when surface mobility is suppressed and the adsorbate species become locked into static ordered structures. During the catalytic hydrogenation of ethylene to ethane in the absence of CO the metal surfaces are covered by an adsorbate layer that is very mobile on the time scale of STM imaging. We found that the addition of CO poisons the hydrogenation reaction and induces ordered structures on the single crystal surfaces. Several ordered structures were observed upon CO addition to the surfaces pre-covered with hydrogen and ethylene: domains of c(4 x 2)-CO+C@sub 2@H@sub 3@, previously unobserved (4 x 2)-CO+3C@sub 2@H@sub 3@, and (2 x 2)-3CO on Rh(111), and a (@sr@19 x @sr@19)R23.4° on Pt(111). A mechanism for CO poisoning of ethylene hydrogenation on the metal single crystals was proposed, in which CO blocks surface metal sites and reduces adsorbate mobility to limit adsorption and reaction rate of ethylene and hydrogen. @FootnoteText@ @footnote 1@ Bartholomew, C. H. App. Catal. A 212, 17-60 (2001).@footnote 2@ Kumbilieva, K., Kiperman, S. L. & Petrov, L. Kinet. Catal. 36, 73-79 (1995).@footnote 3@ Zaera, F. Prog. Surf. Sci. 69, 1-98 (2001).

10:00am **SS1-TuM6 Iridium (210): Nanoscale Faceting and Structure-sensitivity of Surface Reactions***, **I. Ermanoski,** W. Chen, T.E. Madey,* Rutgers University

The stability of the atomically rough fcc Ir(210) surface depends on its cleanliness. The clean surface is planar and unreconstructed after heating in UHV up to 2100K. The oxygen-covered surface is, however, structurally unstable, and undergoes a dramatic faceting transformation: Nanometer-sized pyramids exposing {311} and (110) faces are formed upon deposition of more than 0.5 monolayers of oxygen and annealing to 600K, completely replacing the original planar surface. The oxygen-covered faceted surface reversibly reverts to planar at ~ 900K. LEED and STM experiments show that pyramid sizes increase with annealing temperature, and can reach ~25nm. This growth does not have an effect on the orientation of the facets. The complete thermal desorption of oxygen from iridium requires a temperature of ~1400K, and causes a complete destruction of the faceted structure. Nevertheless, by using catalytic CO oxidation (at ~550K) and reaction of H2 to form H2O (at ~400K), we have been able to routinely prepare a clean faceted surface in situ. Owing to the ability to prepare clean surfaces of different nano-scale structure (planar, faceted, varying facet sizes) from Ir(210), we have found it to be an excellent substrate for studying the kinetics of surface chemical reactions that depend on the surface structure. Our temperature programmed desorption (TPD) experiments show that thermal decomposition of acetylene, hydrogen recombinative desorption and ammonia decomposition all exhibit structure sensitivity, and proceed differently on the planar and faceted surfaces. Furthermore, differences are observed in reactions on clean

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

faceted surfaces with different average facet sizes, showing that particle-size effects also play an important role in these reactions.

10:20am **SS1-TuM7 Kinetics of Co Oxidation Catalyzed by Supported Iridium Particles in a Wide Pressure Range***, **M.M. Sushchikh**, E.W. McFarland,* University of California, Santa Barbara

Recent work in ultra-high vacuum (UHV) has demonstrated kinetic hysteresis in the CO oxidation reaction on single crystal iridium surfaces@footnote 1@,@footnote 2@; the reaction rate variation in CO and O@sub 2@ partial pressures varied depending upon the initial partial pressure. The phenomena observed were explained using a Langmuir-Hinshelwood mechanism. We have investigated the phenomena at elevated pressures on a supported Ir catalyst to test the validity of the model scaled more than 9 orders of magnitude in pressure. It is expected that sticking coefficients at the high surface coverages are not equal to those at lower coverages and as the pressure approaches atmospheric, kinetic phase transitions are affected by changes in the gas composition. Furthermore, on the supported metal particulate catalyst heat transfer effects are more complex. The rate of CO@sub 2@ formation on Ir as a function of reactant pressures (up to 1 atm) was monitored and excellent agreement was found with the UHV experiments. @FootnoteText@ @footnote 1@ S.Wehner, F.Baumann, M.Ruckdeschel, J.Küppers, J.Chem.Phys., 119(13)(2003)6823.@footnote 2@ S.Wehner, F.Baumann, J.Küppers, Chem.Phys.Lett., 370(2003)126.

10:40am **SS1-TuM8 High Pressure Methane Activation on Platinum Single Crystal Surfaces***, **A.L. Marsh**, R.M. Rioux, J.S. Gaughn,* University of California, Berkeley*; G.A. Somorjai,* University of California, Berkeley and Lawrence Berkeley National Laboratory

The interest in alternative sources of energy has generated research on the conversion of hydrocarbons such as methane into hydrogen for both stationary and mobile fuel cell applications. To optimize the processes for the conversion of methane into hydrogen using platinum catalysts, reaction mechanisms must be characterized at a molecular-level. For that reason, we have characterized the high-pressure (up to 40 Torr) activation of methane on platinum single crystal surfaces using infrared-visible sum frequency generation (IR-VIS SFG) spectroscopy and Auger electron spectroscopy (AES). At low temperatures (300 K) and high pressures (1 Torr), methane is activated to form a number of different dehydrogenated intermediates on the Pt(111) surface. The extent of dehydrogenation increases with increasing temperature and pressure. In addition, the amount of carbon deposited on the surface increases with increasing temperature and pressure. Comparisons are made with molecular beam and high pressure experiments on other metal single crystal surfaces to develop a detailed mechanistic picture of the activation of methane at high pressures on platinum catalyst surfaces.

11:00am **SS1-TuM9 Nanoporous Pd Films Grown Via Ballistic Deposition: Structural And Catalytic Properties***, **J. Kim**, Z. Dohnálek, B.D. Kay,* Pacific Northwest National Laboratory

Hydrogenation of ethylene was studied on dense and nanoporous Pd films using molecular beams and temperature programmed desorption (TPD). Porous films were deposited on a Mo(100) substrate at temperatures ranging from 22 to 300 K. Due to limited surface mobility at such low temperatures, the growth is dictated by a ballistic deposition mechanism. The adsorption properties of the films were characterized as a function of Pd deposition angle as well as growth and post-annealing temperatures using N@sub 2@ physisorption. The highest surface area of ~ 80 m@super 2@/g was observed for films grown at 85° and 22 K. Upon annealing to 300 K, the films lose ~40 % of their area, further annealing to 500 K leads to complete densification. Reactivity studies show that nanoporous Pd, covered with H and subsequently saturated with ethylene at 22 K, is highly efficient catalyst for ethylene hydrogenation. This is in sharp contrast with dense Pd films where only trace amounts of ethane were observed. As seen from the reaction yields on films preannealed to various temperatures, the number of catalytically active sites decreases faster than the area of the films. Additionally, cycling of the ethylene hydrogenation reaction also leads to a decrease of ethane production due to poisoning of the active sites.

11:20am **SS1-TuM10 Novel NO Adsorption States on Pd (111) at Elevated Pressures: Irreversibility of the Effects of Temperature and Pressure on Heterogeneous Catalytic Systems***, **E. Ozensoy**[1],* Texas A&M University*; Ch. Hess,* Fritz-Haber-Institut der Max-Planck-Gesellschaft,Germany*; C. Yi,* Texas A&M University*; D. Loffreda,* Institut de Recherches sur la Catalyse, Centre National de la Recherche Scientifique, France*; D.W. Goodman,* Texas A&M Univeristy

NO adsorption states on Pd (111) single crystal model catalyst surface were investigated using in-situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and density functional theory (DFT) calculations within 10@super -9@ - 400 mbar and 25-600 K. Vibrational spectroscopic data and DFT calculations indicate that besides the well-known monomeric NO adsorption states, a novel high-coverage monomeric adsorption state was observed at elevated pressures which was identified to have a (3x3)-7NO structure. NO-dimer states were also determined to exist under both ultra high vacuum (UHV) and elevated pressure conditions, however the nature of the NO-dimers that are formed at low and high pressures were found to be different in terms of their surface coverage, the strength of their interaction with the Pd (111) surface and the intrinsic N-N bond strength. In addition, the formation of dinitrosyls at @theta@@sub NO@ > 0.778 ML was also observed and found to take place only at elevated pressure and temperature conditions suggesting that not all of the thermodynamic equilibrium states at elevated temperatures and pressures are kinetically available at low temperatures and pressures for NO/Pd (111), emphasizing the danger of extrapolating the results of traditional surface scientific experiments performed under to UHV conditions to elevated pressure and temperature cases where the behavior of the system can show remarkable deviations from the expectations.

Surface Science
Room 210C - Session SS2-TuM
Self Assembled Monolayers

Moderator: M. Grunze, University of Heidelberg, Germany

8:20am **SS2-TuM1 Vapor-Phase Adsorption Kinetics of 1-Decene on Hydrogenated Si(111)***, **M.R. Kosuri**, H. Gerung, Q. Li,* University of New Mexico*; S.M. Han,* University of New Mexico, U. S. A.

We have investigated in situ and in real time vapor-phase self-assembly of 1-decene on hydrogenated Si(111), using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The p- and s-polarized IR absorbance of Si-H vibrational mode at 2084 cm@super -1@ strongly supports that the Si(111) surface is terminated with monohydrides prior to 1-decene exposure. The adsorption of 1-decene on hydrogenated Si(111) results in a decane terminated hydrophobic surface, indicated by the sessile-drop water contact angle. X-ray photoelectron spectroscopy is additionally used to determine the temperature dependence on self-assembled monolayer (SAM) formation. The decane SAMs prepared at 80 to 200 °C show an identical saturation surface coverage. The absolute surface coverage, calculated from the IR absorbance of C-H stretching vibrational modes near 2900 cm@super -1@ saturates at 4.3x10@super 14@ cm@super -2@, which translates to 55 % of surface Si atom density. The fractional surface coverage of decane indicates that 1-decene adsorption is a two-step process following a 1st order Langmuir isotherm: (1) fast adsorption with an empirical rate constant k@sub 1@ = 4.2x10@super -2@ min@super -1@ and (2) slow adsorption with an empirical rate constant of k@sub 2@ = 1.6x10@super -2@ min@super -1@. The thickness and cant angle of the decane SAM at the saturation coverage are calculated to be 13 Å and 15° from the surface normal, respectively. In this presentation, we will also discuss the stability of decane SAMs against ambient exposure over time.

8:40am **SS2-TuM2 Molecular Monolayers on Single-Crystal and Nanocrystalline Diamond Surfaces***, **B.M. Nichols**,* University of Wisconsin-Madison*; J.E. Butler, J.N. Russell, Jr.,* Naval Research Laboratory*; R.J. Hamers,* University of Wisconsin-Madison

The chemical stability and electronic properties of diamond make it an attractive substrate for chemical and biological sensing. Recent studies have demonstrated the ability to covalently functionalize nanocrystalline diamond surfaces with molecules bearing a terminal vinyl (C=C) group via a photochemical process under ambient conditions. Here, we report studies of the properties of monolayer films formed on single-crystal diamond(111)

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

and on polycrystalline diamond thin films by this process. XPS measurements on diamond(111) surfaces functionalized with molecules bearing a vinyl group at one end and a fluorine-protected amine group at the other show that the F/C ratio saturates after ~12 hours of reaction, suggesting a self-terminating monolayer. To prove that the molecules are aligned vertically on the surface, we measured the angular dependence of the apparent F/C ratio; this measurement shows that the F atoms are preferentially located at the exposed surface. We find that single-crystal and nanocrystalline samples have similar reaction rates, thereby eliminating the potential role of grain boundaries or graphitic impurities. To characterize the electronic properties, we measured valence-band photoemission spectra and work functions of clean, H-terminated, and molecularly-functionalized diamond(111) surfaces. Our results indicate that the molecularly-modified samples have work functions comparable to the annealed, clean diamond(111) surface, and substantially higher than the H-terminated sample. We will discuss these results and the relationship between the chemical structure, electronic structure, and photochemical functionalization of diamond surfaces.

9:00am **SS2-TuM3 High Resolution Mapping of Compositional Differences and Reactions at Buried Interfaces by Electric Force Microscopy***, H. Takano,* University of Pennsylvania*; G. Edwards, A.J. Bergren, J. Driskell, R.J. Lipert,* ***M.D. Porter,*** Iowa State University **INVITED**

The ability to interrogate the chemical composition of organic films is of vast importance to many areas in interfacial and surface science (e.g., electrocatalysis, corrosion inhibition, organic electronic devices, and biocompatability). This presentation describes two sets of results that demonstrate the ability of electric force microscopy (EFM) to map compositional differences of organic monolayers buried under thick polymer films. The first example examines the compositional mapping of organic monolayers buried under an ~430 nm film of polystyrene. The underlying adlayer was patterned onto a gold surface using the microcontact printing of CH3(CH2)16SH followed by solution deposition of HO(CH2)16SH. This procedure results in alternating domains of different terminal groups. Results show that the imaging mechanism exhibits sufficient contrast to function as a mapping methodology for buried functional groups. The second example presents the results from monitoring photochemical reactions of polymeric films deposited on organic monolayer-covered metal substrates. UV-light was irradiated on the polymer/monolayer/metal composites through a photomask, resulting in alternating domains. These findings show not only that EFM can distinguish the domains of reacted and non-reacted portions, but also that EFM can provide sufficient contrast as a subsurface mapping technique. Issues related to the imaging mechanism are also examined. Models that explore the fundamental basis of this capability are also discussed.

9:40am **SS2-TuM5 Chemical Engineering of GaAs Surfaces with Aromatic Self-Assembled Monolayers***,* ***M. Zharnikov****, A. Shaporenko,* Universität Heidelberg, Germany*; K. Adlkofer,* Technische Universität München, Germany*; A. Ulman,* Polytechnic University*; M. Tanaka,* Technische Universität München, Germany*; M. Grunze,* Universität Heidelberg, Germany

Stochiometric GaAs (100) surfaces were functionalized with monolayers of non-substituted and substituted thiol-derived aromatic compounds and the engineered surfaces were studied by several complementary experimental techniques including synchrotron-based high resolution x-ray photoelectron spectroscopy and near edge x-ray absorption fine structure spectroscopy. The aromatic molecules were found to form well ordered and densely packed self-assembled monolayer on these substrates. The attachment to the substrate occurs over the thiolate headgroup while the intact aromatic chains have an upright orientation with an average tilt angle of about 30°. The functionalization of GaAs was found to prevent an oxidation and contamination of the substrate, keeping the GaAs surface in a pristine state. In addition, the wetting properties of this surface could be controlled by the selection of a suitable substitution, e.g. methyl or hydroxy group. The surface engineering of GaAs with functionalized aromatic monolayers can provide a crucial link for combining GaAs-based heterostructures and devices with bio-organic molecular assemblies.

10:00am **SS2-TuM6 Self Assembled Monolayers of Arenethiol Molecules on Cu(111)***,* ***K. Wong****, K.-Y. Kwon, B.V. Rao, A. Liu, L. Bartels,* University of California, Riverside

The utility of the thiol group on anchoring organic molecules to metal surfaces has been widely recognized. The thiol group makes sufficiently strong bonds with the metal substrate that stable monolayers are formed spontaneously even at room temperature in a solution environment. At low coverages and under ultra-high vacuum conditions isolated thiols exhibit significant surface mobility even at temperatures as low as 80K. We have studied monolayers of thiolphenol (TP) molecules and several halogen substituted para-X-TP derivates (where X is Br, Cl or F) at various coverages. All TPs adsorb with the benzene ring parallel to the surface and do not tilt to a vertical orientation as long as there is sufficient surface area available to accommodate all adsorbed molecules in a horizontal fashion. At such coverages we find a pronounced dependence of the ability of the TPs to form ordered films on the nature of their substitution. The most remarkable differences were found at incomplete coverage where the molecules have space to rearrange themselves into the optimal surface conformation and are not exposed to lateral stress. X-TP molecules form patterns of various degrees of complexity: Br-TP forms a simple (3x4) structure with one molecule per unit cell. Cl-TP films are made up of slightly more complicated unit cells involving two neighboring molecules whose sulfur atoms are located in different (hcp and fcc) Cu(111) hollow sites. F-TP molecule self assemble into a (8x8)R19@super o@ honeycomb pattern consisting of seven molecules per unit cell. Unsubstituted TP and pentafluoro-TP do not form any extended ordered patterns. This suggests that differences in the chemical properties between the para- and the meta-/ortho- substituents of TPs play a crucial role in the pattern formation process. We present a model based on quadrupolar intermolecular interaction to account for these observations.

10:20am **SS2-TuM7 Fabricating Self-Assembled Monolayers of Selenolates on Noble Metal Substrates***,* ***A. Shaporenko,*** Universität Heidelberg, Germany*; A. Ulman,* Polytechnic University*; A. Terfort,* Universität Hamburg, Germany*; M. Grunze, M. Zharnikov,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of selenolates can be considered as an alternative to thiolates for fabricating SAMs on noble metal surfaces. To prove this approach, we applied a standard immersion procedure to prepare SAMs from several aliphatic and aromatic selenide and diselenide compounds on gold and silver substrates. The resulting films were characterized by several complementary experimental techniques including infrared refection-absorption spectroscopy (IRRAS), synchrotron based high-resolution X-ray photoelectron spectroscopy (HRXPS), near edge X-ray absorption fine structure spectroscopy, and contact angle measurements. The results suggest a dissotiative mode of monolayer formation from diselenide compounds on both gold and silver. However, in the case of long chain alkylselenides and dialkylselenides, no high quality films were formed. In the case of short chain alkylselenides, semifluorinated alkylselenides, and biphenylselenides, well-defined and densely packed SAMs were fabricated. Only one selenium species, namely selenolate was found in all above-mentioned films on the basis of the Se3d HRXPS spectra. Distinct C1s photoemission peaks were observed and related to well-defined aliphatic or aromatic chain. Characteristic IR absorption bands and X-ray absorption resonances corresponding to intact molecular chains of definite conformation were observed. The information on molecular orientation and packing density was derived.

10:40am **SS2-TuM8 Interface Electronic Structure of Thiol Terminated Molecules on Metals***,* ***A.N. Caruso****, L.G. Wang, E.Y. Tsymbal, S.S. Jaswal, P.A. Dowben,* University of Nebraska

Thiol terminated molecules may be useful to both molecular electronic and spintronic applications. The orientation and electronic properties of biphenyldimethyldithiol (S-CH@sub 2@-C@sub 6@H@sub 4@-C@sub 6@H@sub 4@-CH@sub 2@-S) adsorbed on Au(111) and polycrystalline cobalt are identified from combined polarization dependent photoemission and inverse photoemission. The stable orientation, bonding site and electronic properties of methylthiolate (S-CH@sub 3@) adsorbed on Au(111) and Co(0001) are found by density functional calculations. Both experiment and theory show a stronger bonding to cobalt over gold surfaces for both thiol terminated molecules. Calculated charge transfer with the substrates to and from the sulfur further confirms bonding and reasoning behind the experimentally found highest occupied to lowest unoccupied molecular orbital gap offset from the Fermi level. Calculations also show that the three-coordinated fcc and hcp hollow sites are most stable for methylthiolate adsorption.

11:00am **SS2-TuM9 Designing Self-assembled Monolayers (SAM) of Thiols: A Study on Lattice Mismatch***, P. Cyganik,* ***M. Buck,*** St Andrews University, UK*; C. Woell,* Ruhr-Universitaet Bochum, Germany

Applications of self-assembled monolayers (SAM) of thiols in, e.g., molecular electronics or electrochemistry are crucially dependent on the extent to which their properties can be controlled. Besides the control of the molecular electronic properties, controlling the structure, i.e., defects and crystallinity, is an issue of equal importance. As for any adsorbate system tailoring of SAMs has to address mismatch between molecular and substrate lattices. Surprisingly, this aspect which is of fundamental importance toward a controlled design of thiol SAMs has received very little attention. The talk presents STM studies on biphenyl based thiols which are characterized by an alkane spacer between the sulphur head group and the aromatic moiety. Within a homologue series of these biphenyl thiols with the spacer varying from 0 to 6 methylene units, intermolecular interactions, molecular orientation, and, thus, packing of the molecules are substantially changing. Contrast variations in scanning tunneling microscopy images reveal lattice mismatch. The way mismatch is accomodated depends strongly on the alkane spacer and, therefore, the achievable structural perfection is varying across the homologue series. The results suggest that a flexible spacer acts as a buffer layer which can accomodate mismatch between the lattice of aromatic moieties and the substrate lattice.

11:20am **SS2-TuM10 Sulfur-induced Nano-restructuring of the Au(111) Surface: A Real-time STM Study***, **M.M. Biener,*** Harvard University*; J. Biener,* Lawrence Livermore National Laboratory*; D. Pinnaduwage, C.M. Friend,* Harvard University

The interaction of sulphur with gold surfaces has attracted considerable interest due to numerous technological applications such as the formation of self-assembled monolayers (SAMs), corrosion inhibition, and sensors. In this work, the interaction of sulfur with Au(111) was studied by real-time scanning tunnelling microscopy (STM) using sulfur dioxide as a source of sulfur. A small fraction of the impinging sulfur dioxide molecules deposit sulphur on the surface. Up to a coverage of ~0.3 ML sulfur forms an ordered adlayer. With further increasing S coverage we observe the formation of a two-dimensional AuS overlayer exhibiting short range order. Gold atoms are removed from the surface and are incorporated into the growing gold sulfide resulting in pit formation. This gold sulfide layer is stable up to ~500 K where it develops long-range order and exhibits a complex Low Energy Electron Diffraction (LEED) pattern. We will present nano-scale, time-resolved movies capturing the sulphur induced restructuring of the Au(111) surface.

11:40am **SS2-TuM11 Comparative UHV-STM Study of Adsorption Structures Formed from a Family of Oligo(phenylene ethynylene)s on Au(111)***, L. Petersen, C. Busse, S. Terkelsen, **T.R. Linderoth**, M. Nielsen, K.V. Gothelf, F. Besenbacher,* University of Aarhus, Denmark

To realize the goal of functional structures formed by molecular self-assembly, systematic studies of factors directing the assembly process are required. Using UHV-STM we have performed a comparative study of adsorption structures formed by a family of structurally different, but chemically similar, organic molecules adsorbed on the Au(111) surface. The molecules consist of a central benzene ring with three or two acetylene spokes (para, meta, or ortho) leading to highly conjugated pi-systems of three-spoke, linear, bent, or v-shaped molecular geometry. Each spoke terminates in a tert-butyl substituted salicylaldehyde moiety. Upon adsorption at room temperature (and imaging at ~150 K to reduce molecular mobility), a variety of close-packed phases are observed, most of which can be rationalized by a common motif of molecules adsorbed with their backbone parallel to the surface and with optimized intermolecular side-to-side interaction, most likely through van der Waals coupling. Interesting exceptions to this picture are the linear molecules, which in addition form a more open nano-grid type structure thought to be dominated by intermolecular hydrogen bonding, and the v-shaped molecules where a reduced footprint indicates non-planar adsorption geometry. The described results constitute a platform for ongoing experiments where (i) similar molecules with systematically altered functional moieties are used, e.g. disabling or further encouraging intermolecular hydrogen bond formation, (ii) structures formed through co-adsorption with transition metals (Ni,Fe) are investigated, and (iii) intermolecular covalent cross-linking is induced through co-adsorption with reactive diamines.

Surface Science
Room 210B - Session SS1-TuA

Hydrocarbon Reactions on Metal Surfaces

Moderator: D.E. Barlow, Naval Research Laboratory

1:20pm **SS1-TuA1 Thermodynamics and Kinetics of Elementary Steps on Surfaces, and their Applications in Modeling Complex Reactions***, **C.T. Campbell**,* University of Washington **INVITED**

Some useful concepts for describing elementary reaction steps on surfaces will be reviewed, and illustrated with example applications to catalytic reactions. First, the characteristics which define a true "elementary step" will be considered. In general, the reaction order is well defined for true elementary steps, and their prefactors can be theoretically estimated with reasonable accuracy using transition state theory and simple concepts of statistical mechanics. Once the prefactor is known, a single absolute rate measurement provides the activation energy, which is thus obtained with good accuracy even when the prefactor used is in error by two orders of magnitude. The net reaction energy often can be measured independently. Examples of doing this with adsorption calorimetry will be reviewed. Recent developments promise to make calorimetric measurements of adsorption energies on single crystal surfaces more common, since they now can be applied to crystals as thick as obtainable by simple mechanical thinning (80 ï⍰-m). Once the net reaction energy is known for an elementary step, a measurement of its activation energy directly provides that for its reverse step and, through knowledge of statistical mechanics, its equilibrium constant. These kinetic and thermodynamic parameters are invaluable in examining or modeling the rates of complex reaction mechanisms, which in general turn out to depend on the kinetic and thermodynamic parameters of only a few of the many elementary steps involved. A simple method for determining which of the elementary steps are critical, based on the â?odegree of rate controlâ?⍰, will be described. Work supported by DOE-OBES and NSF.

2:00pm **SS1-TuA3 Recent Advances in the Surface Chemistry of Hydrocarbon Fragments on Transition Metals***, **F. Zaera**,* University of California

A brief review of recent results from our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. The chemistry of C4 hydrocarbons on Pt(111) single-crystal surfaces will be highlighted, with focus on the steps responsible for double bond migration and cis-trans isomerization in olefins. A comparison will be provided with our previous studies using shorter moieties, and the role of different key intermediates such as alkyls and allyls will be discussed. Insertion reactions will be addressed next. Specifically, the mechanism of chain growth on Ni(110) surfaces will be analyzed in terms of the chemistry of methylene and methyl on that surface. The effect of coadsorbed oxygen on these reactions, as well as the opening of new oxygen incorporation steps, will be discussed. Finally, reference will be made to the surface chemistry of chiral compounds on metals as it relates to enantioselective catalysis.

2:20pm **SS1-TuA4 Enantioselective Reactivity of R-2-bromobutane on Chiral Copper Surfaces***, **D.M. Rampulla**, A.J. Gellman,* Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. Enantioselective reactions require chiral media such as solvents, surfaces, or catalysts of a single handedness. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(643)@super R@ and Cu(643)@super S@ surfaces. Alkyl halides, such as R-2-bromobutane adsorb dissociatively to form R-2-butyl groups, which decompose via @beta@-hydride elimination to yield 1- and 2-butenes. The temperatures at which these desorb and the selectivity to 1- and 2-butenes are influenced by the chirality of the copper surfaces. Earlier results of R-2-bromobutane on Cu(531)@super R&S@ surfaces will be discussed and compared with more recent results obtained on the Cu(643)@super R&S@ surfaces.

2:40pm **SS1-TuA5 Stereochemistry in Surface Explosion***, **K.-H. Ernst**, B. Behzadi, R. Fasel, S. Romer,* EMPA Duebendorf, Switzerland

The vast majority of chiral compounds crystallize into racemic crystals. It has been predicted early and was later experimentally established as a rule, that chiral molecules on surfaces are more easily separated into homochiral domains due to confinement into a 2D-plane and lower entropic contributions. We investigated the formation and stability of two-dimensional tartrate lattices on a Cu(110) surface for the racemic mixture by means of temperature programmed desorption (TPD), low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). At low coverage, the bitartrate species becomes separated into homochiral domains, but with increasing surface density the monotartrate species forms a closed-packed racemic 2-D crystal. Consequently, the 2-D conglomerate bitartrate phase does not show differences to the enantiopure bitartrate phase with respect to thermal stability. However, the thermally induced autocatalytic decomposition reaction, so-called surface explosion, of the monotartrate species is influenced by the chirality of the adjacent molecules. The racemic mixture undergoes decomposition at a lower temperature than the enantiopure lattice at same coverage and lateral arrangement. This is in contrast to the higher stability of 3D tartaric acid crystals, but is consistent with the observation that homochirality is preferred in hydrogen-bonded self-assembled biomolecular structures.

3:00pm **SS1-TuA6 The Ullmann Coupling Reaction: Atomic Scale Study of the Reactive Intermediates and Products of a Surface Catalyzed Reaction***, **S.U. Nanayakkara**, E.C.H. Sykes, L.C. Fernández-Torres, P. Han, P.S. Weiss,* The Pennsylvania State University

We present an atomic-scale study of the Ullmann coupling reaction on Cu{111} using low temperature scanning tunneling microscopy and spectroscopy. We have studied the reactive intermediates and the products of the Ullmann coupling reaction between bromobenzene molecules, which form biphenyl at room temperature (293 K). Chemical identification of the surface-bound species has been achieved using their tunneling spectroscopic signatures. We demonstrate that bromobenzene molecules dissociatively chemisorb at 293 K and form phenyl intermediates, which travel distances of up to a few 1000 @Ao@ over Cu{111} terraces to bind preferentially at step edges. This preference is due to the anisotropic electron density distribution at the step edges. We identify the surface step edge as the active site of this reaction on Cu{111} for C-C bond formation. Once two phenyl intermediates combine to form biphenyl, these product molecules diffuse onto the terraces and arrange as clusters. Our interpretations of the preferred adsorption sites and the intermolecular interactions of adsorbates are explained in terms of the local electronic perturbations on the surface by surface steps and adsorbates.

3:20pm **SS1-TuA7 Adsorption Energies of Small Alkane Molecules on MgO(100), Pt(111), and C(0001)/Pt(111) by Temperature Programmed Desorption***, **S.L. Tait, Jr.**,* University of Washington*; Z. Dohnálek,* Pacific Northwest National Laboratory*; C.T. Campbell,* University of Washington*; B.D. Kay,* Pacific Northwest National Laboratory

The adsorption of small hydrocarbon molecules at oxide and metal surfaces represents an important scientific problem with applications in catalysis and sensors. We have used molecular beams and temperature programmed desorption (TPD) to study the adsorption of small alkane molecules, C@sub n@H@sub 2n+2@ (n=1-10), on MgO(100), Pt(111), and a two-dimensional graphite film on Pt(111). Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined incident angle and kinetic energy. The adsorption energies and pre-exponential factors are extracted from TPD data. Simulations based on the results of this analysis show excellent agreement with experiment. The desorption prefactors increase with alkane chain length by more than five orders of magnitude over the range of alkane molecules studied. Adsorption energy on each surface increases linearly with alkane chain length with a y-intercept value near zero. Prior studies have found a non-zero intercept by treating the pre-exponential factor as constant with alkane chain length. This increase in pre-exponential factor can be attributed entirely to the increase in the rotational entropy in the transition state theory, assuming that the adsorbed initial state is not a free rotor but that the transition state is. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

3:40pm **SS1-TuA8 Characterization of Ethylidene and Methylidyne on Pt(111) with Infrared Spectroscopy***, **R. Deng**, E. Herceg, M. Trenary,* University of Illinois at Chicago

Hydrocarbon intermediates formed in the adsorption and decomposition of ethylene (C@sub 2@H@sub 4@), diiodomethane (CH@sub 2@I@sub 2@) and iodomethane (CH@sub 3@I) on Pt(111) were investigated using reflection absorption infrared spectroscopy (RAIRS) and mass spectrometry. The ethylidene (CHCH@sub 3@) species is identified on the basis of RAIRS peaks at 2960 cm@super -1@ and 1387 cm@super -1@ that are assigned to the CH@sub 3@ asymmetric stretch and the CH@sub 3@ symmetric bend, respectively. It is found that the highest ethylidene coverage can be produced by ethylene exposure to the surface at temperatures around 280 K. Ethylidene undergoes rapid hydrogenation upon exposure to 2x10@super -7@ Torr of H@sub 2@ at 250 K to produce gas phase ethane, as detected by a mass spectrometer. The results indicate that ethylidene could be an intermediate in ethylene hydrogenation on transition metal surfaces near room temperature. Surface methylidyne can be formed in multiple ways: thermal decomposition of diiodomethane and iodomethane; ethylene decomposition at a temperature of about 500 K; and surface carbon hydrogenation. Methylidyne is identified by a CH (CD) stretch mode at 2956 (2206) cm@super -1@. The co-adsorption of surface hydrogen and iodine causes this band to shift to higher frequency. The observation of methylidyne at 500 K indicates that C-C bond scission of the initially adsorbed ethylene occurs at this temperature.

Surface Science
Room 210C - Session SS2-TuA
Welch Award Symposium: Nucleation and Growth

Moderator: P.J. Feibelman, Sandia National Laboratories

1:20pm **SS2-TuA1 Real-Time Microscopy of Second Order Phase Transitions on Pb/Ge(111)***, **Y. Sato**, S. Chiang,* University of California, Davis

Using the Low Energy Electron Microscope (LEEM), we have studied phase transitions that occur on the Pb/Ge(111) surface. We have observed a very unusual second order phase transition with strong fluctuations at coverages above 1ML. The Pb layer forms two stable (@sr@3x@sr@3)R30° phases on the surface, a low-density @alpha@ phase and a dense @beta@ phase. It is well known that the critical temperature of the phase transition from @beta@ to (1x1) depends strongly on the coverage. The transition occurs at 180C for coverage below 1ML and at 270C for coverages above 1.33ML. LEEM data clearly show this difference in the critical temperature derives from the different mechanisms of the transformation. For coverages between 0.33ML and 1ML, where the @alpha@ phase coexists with the @beta@ phase below the critical temperature and with the (1x1) phase above it, the reversible phase transformation from @beta@ to (1x1) shows typical second order phase transition behavior, i.e., the intensity of the @beta@ phase gradually changes with temperature. On the other hand, for coverages above 1 ML, where the surface is either the low temperature @beta@ phase or the higher temperature (1x1) phase, the system shows an unusual second order phase transition. As the sample is heated through the critical temperature, the (1x1) phase appears as small domains over the surface. The domains appear and disappear until they are stabilized in the new phase. The transition is reversible, and similar behavior is observed upon cooling. The frequency analysis of the critical fluctuations will be presented, and the different mechanisms for both of the second order phase transitions mentioned above will be discussed.

1:40pm **SS2-TuA2 Dislocation-Driven Surface Dynamics on Solids***, **S. Kodambaka**, S.V. Khare, J. Bareno, W. Swiech, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. We observe, in real time, the thermally-driven (1500-1700 K) nucleation and shape-preserving growth of spiral steps rotating at constant temperature-dependent angular velocities (@omega@(T)) around cores of dislocations terminating on TiN(111) in the absence of applied external stress or net mass change. We measure @omega@ as a function of spiral geometry, N@sub2@ partial pressure, annealing time, and temperature. We find that @omega@ is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent @omega@ data, we obtain an activation barrier of 4.9±0.3 eV for the growth of spirals. This phenomenon, attributed to point-defect migration from the bulk to the surface along dislocation lines, is both qualitatively and quantitatively different from step curvature-driven surface dynamics and "standard" Burton-Cabrera-Frank (BCF) spiral growth.@footnote 1@ Our results demonstrate that dislocation-mediated surface roughening can occur even in the absence of deposition or evaporation, and provide fundamental insights into mechanisms controlling nanostructural stability. We expect that this process is general and that it occurs in other materials.@footnote 1@ S. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, Nature, May 6th issue, 2004.

2:00pm **SS2-TuA3 Probing the Kinetics of Nanoscale Self-Assembly on Surfaces***, **G.L. Kellogg**,* Sandia National Laboratories, US **INVITED**

Pb atoms deposited on Cu(111) form a Pb-poor surface-alloy phase and a Pb-rich overlayer phase which spontaneously order into nanoscale domain patterns.@footnote 1@ The thermodynamic forces responsible for the self-assembly have been determined in previous studies with the LEEM.@footnote 2@. In this talk I will describe recent studies of the atomic mechanisms underlying the remarkable cooperative motion that allows these patterns to form and evolve. For example, the ordering of Pb overlayer islands occurs by islands containing 10's of thousands of atoms moving 100's of nm's is a few minutes. To help understand the atomic processes responsible for such motion, we measured the thermal decay of pure Cu, Pb-overlayer, and Pb/Cu surface-alloy islands using both STM and LEEM.@footnote 3@ The results indicate that the diffusion of Cu atoms over the Pb-Cu surface alloy is rate-determining for the decay both Pb overlayer and Pb-Cu alloy islands and that slower diffusion on the surface alloy is due to path blocking by embedded Pb atoms. Additional LEEM studies of Cu island nucleation within the Pb overlayer strongly suggest that the large-scale mobility of overlayer islands is accomplished by fast migration of Cu atoms within the overlayer. Thus, the rapid self-assembly in this system can, surprisingly, be traced to the existence of a low energy Cu thermal defect within the Pb overlayer. Sandia is operated by Sandia Corporation, a Lockheed Martin company, for the U. S. Department of Energy under Contract #DE-AC04-94AL85000. @FootnoteText@ @footnote 1@ R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature 412, 875 (2001).@footnote 2@ R. van Gastel, R. Plass, N. C. Bartelt, and G. L. Kellogg, Phys. Rev. Lett. 91, #55503 (2003); R. van Gastel, N. C. Bartelt, P. J. Feibelman, Francois Leonard, and G. L. Kellogg, Phys. Rev. B, submitted.@footnote 3@ M. L. Anderson, N. C. Bartelt, P. J. Feibelman, G. L. Kellogg, and B. S. Swartzentruber, in preparation.

2:40pm **SS2-TuA5 Medard Welch Award Presentation: Growth and Epitaxy of Thin Pentacene Films***,* **INVITED**

Pentacene (Pn) is the highest mobility organic semiconductor known. It is a crystalline organic solid that can be deposited on a substrate by either vacuum sublimation, or by spin coating of a suitable soluble precursor followed by mild annealing. In this talk I will focus on studies of Pn thin film growth in vacuum, studies by in-situ Low Energy Electron Micrcopy, Scanning Tunneling Microscopy, and Photo Electron Spectroscopy. We find that the molecular orientation in the growing film, as well as the nucleation density depend strongly on the choice and preparation of the substrate. For instance, grain sizes can vary from 0.1 micrometer to over 0.1 millimeter. Molecules can orient in-plane or out-of-plane, depending on the electronic structure of the substrate. On most substrates, grains show random azimuthal orientation, but recently we have succeeded in growing epitaxial pentacene films on a number of different substrates that hold promise for the fabrication of epitaxial organic thin film transistors with improved transport properties. In this talk I will review our results and recent progress.

3:20pm **SS2-TuA7 Growth Dynamics of Organic Semiconductors***, **F. Schreiber**,* Oxford University, UK **INVITED**

We will review our recent work on the growth dynamics of molecular semiconductors by organic molecular beam deposition (OMBD), with emphasis on growth studies beyond the first monolayer, i.e. the evolution of the film structure and morphology. After briefly discussing general issues related to growth modes, correlation functions, dynamic scaling, and growth exponents, we will try to identify the general features that distinguish organic from inorganic systems, such as the different interaction potentials and the internal degrees of freedom of organic molecules.@footnote 1@ We will then discuss selected case studies of perylene-derivatives (in particular diindeno-perylene (DIP)@footnote 2@ and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)@footnote 3@), with results on the dynamic scaling exponents and real-time studies of the growth. Finally, we will briefly discuss the implications for organics-based heterostructures and the improvement of device performance. @FootnoteText@@footnote 1@F. Schreiber, Phys. Stat. Sol. (a) 201 (6) (2004) 1037 @footnote 2@A. C. Dürr et al., Phys. Rev. Lett. 90 (2003) 016104 @footnote 3@B. Krause et al., Europhys. Lett. 65 (3) (2004) 372

Surface Science
Room Exhibit Hall B - Session SS-TuP
Poster Session

SS-TuP1 HREELS and TPD Investigation of Electron Irradiation Effects on Diethylsilane-Covered Si(100) Surfaces at 100K*, **J. Lozano**, D. Early, J.H. Craig, Jr., P. Wang, K.R. Kimberlin,* Bradley University

The effects of 600-eV electron irradiation of diethylsilane (DES) adsorbed on Si(100) was studied using high-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption. The effects of electron irradiation at submonolayer and multilayer DES coverages will be discussed. Previous electron stimulated desorption and TPD studies suggested an electron-induced beta hydride elimination process as a pathway for ethyl group desorption at 100K. The results of HREELS experiments performed to probe such processes will be discussed.

SS-TuP2 FTIR and XPS Studies of Porphyrin Containing Monolayers on Si(100) Surfaces*, **D.A. Syomin**, A.A. Yassery, F. Zaera, D.F. Bocian,* University of California Riverside

A number of mono-coordinated monolayers of redox-active Zn-containing porphyrins with a variety of organic linkers were prepared by thermal assembly onto hydrogen-terminated Si(100) surfaces. The porphyrin monolayers were characterized using attenuated total reflection (ATR) infrared and X-ray photoelectron spectroscopy (XPS) as well as standard electrochemical methods. The molecular orientation of the adsorbates within the monolayer films as a function of molecular coverage and type of organic linker used was investigated.

SS-TuP3 STM Study of Phosphine Adsorption on Si(111)-7x7 Surfaces*, **J.-Y. Ji**, T.-C. Shen,* Utah State University

PH@sub 3@ reaction with Si(111) surfaces has been studied by Yates et al. and Avouris et al. using a number of analytical techniques including UPS, AES, EELS and ESD in 1990. They concluded that PH@sub 3@ adsorbs dissociatively at 100 K and the surface is chemically inert. We are interested to revisit this system because the P-delta layer in the (111) direction may have interesting technological implications. In this report we present real space images of the PH@sub 3@ adsorption on Si(111)-7x7 at room temperature for various exposures between 0.3-60 L. Applying different sample biases we identify reacted and unreacted adatom sites. Similar to the ammonia adsorption, we find that center adatoms are more reactive than corner adatoms. However, careful analysis shows three different types of reacted sites which can be considered as PH@sub 3@, PH@sub 2@, and H adsorption sites. The coverage counting of the species suggests that most of PH@sub 3@ is dissociatively adsorbed on the surface at initial exposure generating H and PH@sub 2@ adsorption sites, followed by molecular adsorption of PH@sub 3@. Issues involving dissociation and desorption stimulated by electrons, saturation coverage at different substrate temperatures, and surface structures after annealing will be discussed. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

SS-TuP5 Irradiation Effects of Undulator Synchrotron Radiation Beam on Hydrogen-Terminated Si (111) Surfaces Studied by STM*, **Y. Nonogaki**, T. Urisu,* Institute for Molecular Science, Japan

Undulator synchrotron radiation (USR) is a powerful light source for observation of surface VUV-photochemical reactions, since it is quasi-monochromatic and has high photon flux. It is also very attractive for semiconductor device processes using photochemical reaction. We have designed and constructed a beamline for surface photochemistry and nanofabrication of semiconductor at the UVSOR facility. Using this beamline hydrogen desorption on hydrogen-terminated Si (111) surfaces (H-Si (111)) was investigated using the USR and STM observation. We successfully observed that H-Si (111) was drastically changed after the USR irradiation. H-Si (111) was prepared with atomic H exposure to Si (111) 7x7 at surface temperature of 350°C for 10 min. The H-Si (111) was exposed to the USR at room temperature for 5 to 60 sec, where 1st harmonic of the USR was centered at 100 eV. Correspondent irradiation dose is 1000 to 10000 mAsec (ring current x time). STM observation was performed with tungsten tips at room temperature. STM observation of H-Si (111) showed that there were adatom islands and small protrusions on rest-atom monohydride surface. The adatom islands have triangular shape and bilayer height typically, of which coverage was ~15%ML. On the rest-atom monohydride surface, extension of unfaulted regions were observed and faulted regions was ~20%ML. Surface morphology was changed after USR irradiation. Density of the small protrusions significantly increased with irradiation dose from 1.4%ML at 0 mAsec to 12.8%ML at 10000 mAsec. The distribution of small protrusions were random whether on unfaulted and faulted region. The rest-atom monohydride surface seems to be unchanged. The small protrusions are assigned to dangling bond formed by irradiation-stimulated H-desorption from the rest-atom monohydride on the surface.

SS-TuP6 Theoretical and Experimental Comparison Studies of the Electronic Structure of Molecular Carborane Films*, **S. Balaz**, L.G. Rosa, A.N. Caruso, J.I. Brand,* University of Nebraska-Lincoln*; Y.B. Losovyj,* Louisiana State University*; P.A. Dowben,* University of Nebraska-Lincoln

Semiconducting boron carbide represents a new class of semiconductoing materials with applications in neutron detection and radioactive decay calorimetry [1,2]. The key to making a good boron carbide semiconductor requires materials fabrication by chemical vapor deposition (usually with plasma, electron beam, or synchrotron radiation assisted decomposition of the molecular precursor). The properties of the semiconducting boron carbide appear to be intimately connected to the source compound used. There is no obvious reason why different isomers of the closo-carborane, dicarbadodecaborane C@sub 2@ B@sub 10@H@sub 12@, should result in such different semiconducting properties [2,3]. Utilizing the synchrotron photoemission, and exploiting photovoltaic charging as a test of the n-type and p-type semiconductor behavior [4], during the deposition process, is key to developing the necessary understanding. Theory suggests little difference in electronic structure but profound differences are observed in experiment. Theoretical calculations from semiempirical calculations of the isolated 1,2 closo-carborane (orthocarborane) and 1,7 closo-carborane (metacarborane) molecules indicate that these isoelectronic carboranes should be very similar in HOMO-LUMO gap (highest occupied - lowest unoccupied molecular orbital). These calculations predicted 10.97 eV for the orthocarborane and 10.87 eV for the metacarborane. Since the two carboranes differ only in the positions of the two included carbon atoms and theory predicted the electronic states to be so close, great similarity in chemical and physical behavior would be expected, but is not observed. @FootnoteText@ [1]Robertson et al.,JP APL 80(19): 3644-3646 (2002) [2]A. N. Caruso et al., Journal of Physics Condensed Matter 16, L139 (2004) [3]A. N. Caruso et al., APL 84, 1302 (2004) [4]J.E. Demuth et al., Phys. Rev. Lett. 56, 1408-1411 (1986)[5]A.P. Hitchcock et al. J. Phys. Chem. B 101, 3483 (1997) .

SS-TuP8 Scanning Tunneling Microscopy Study of GaCrN Grown by MBE*, **M.B. Haider**, H.A. Al-Brithen, R. Yang, C. Constantin, D. Ingram, A.R. Smith,* Ohio University

According to Sato et al., (Ga,Cr)N is expected to show ferromagnetism above room temperature if the bulk Cr@sub Ga@ concentration is above 2%.@footnote 1@ Although many (mainly bulk) techniques have been applied to study dilute magnetic nitride systems here we apply in situ STM to investigate issues of Cr incorporation, Cr diffusion/segregation, and the effects of growth parameters. Cr-doped GaN(000-1) has been grown using rf-plasma MBE on sapphire (0001) at Ts ~ 700°C. The Ga/N flux ratio has been varied from 65-100% with variable Cr/Ga flux ratio between 3-11% for GaCrN growth. Based on the Ga/N flux ratio, three growth regimes were found: N-rich, metal-rich, and Ga-rich. It was found that under all three conditions GaCrN surfaces are smoother even to atomistic level forming 3x3 reconstructions after the growth as revealed by RHEED and AFM. This is in contrast to Ga-polar GaMnN case, where N and metal-rich surfaces are not smooth and under Ga-rich conditions Mn droplets of micron size are formed due to the Ga bilayer which exists during Ga-rich GaN(0001) growth.@footnote 2@ Atomic scale STM images of Ga-rich GaN(000-1) covered with 0.05ML of Cr deposited at 700°C show 3x3 and 6x6 reconstructions indicating the presence of Cr atoms within the surface structure. STM images of GaN(000-1) with Cr deposition of 0.2ML and above show some linear features suggesting transition from Cr substitution to 2nd order phase nucleation at the surface. The 3x3 reconstructions have been observed upon exposure of GaN(000-1) 1x1 to Cr at room temperature by RHEED and STM. These STM images suggest that on GaCrN surface, at low Cr concentration, Cr occupies Ga position. Another interesting phenomenon of contrast reversal of 3x3 and 6x6 reconstructions has been observed by STM on 5% Cr doped GaN(000-1) surface, which depends on the tip condition. @FootnoteText@ @footnote 1@Sato et al. J. Superconduc, 16 (2003) 31@footnote 2@Haider et al. J. Appl. Phys., 93 (2003) 5274.

SS-TuP9 Spatial Persistence and Survival Probabilities for Fluctuating Interfaces*, **M. Constantin**, S. Das Sarma,* University of Maryland*; C. Dasgupta,* Indian Institute of Science, India

We report the results of numerical investigations of the steady-state (SS) and finite-initial-conditions (FIC) spatial persistence and survival probabilities for (1+1)-dimensional interfaces with dynamics governed by the nonlinear Kardar-Parisi-Zhang (KPZ) equation and the linear Edwards-Wilkinson (EW) equation with both white (uncorrelated) and colored (spatially correlated) noise. We study the effects of a finite sampling distance on the measured spatial persistence probability and show that both SS and FIC persistence probabilities exhibit simple scaling behavior as a function of the system size and the sampling distance. Analytical expressions for the exponents associated with the power-law decay of SS and FIC spatial persistence probabilities of the EW equation with power-law correlated noise are established and numerically verified.

SS-TuP10 Sublimation Behavior of SiO@sub 2@ from Low and High-Index Si Surfaces Studied by Atomic Force Microscopy*, **J.C. Moore**, A.A. Baski,* Virginia Commonwealth University

We have used atomic force microscopy (AFM) to investigate the sublimation behavior of 100-nm thick oxide layers on the low-index Si(001) and high-index Si(5 5 12) surfaces. During high vacuum anneals, we have observed the formation of holes that nucleate at defects and grow laterally with annealing time (1 to 4 min, 1150@degree@C to 1350@degree@C). The depth of these holes is ~200 nm, or approximately twice the thickness of the oxide film. This is consistent with the thermal decomposition of SiO@sub 2@, where Si is extracted from the bulk in equal ratio to SiO@sub 2@ in order to form volatile SiO. As expected, the lateral growth of these holes is linear with annealing time (2 @micron@/min for 1200@degree@C). Interestingly, it is possible to obtain hole diameter data vs. annealing time by performing sequential anneals in vacuum, and then observing by AFM the formation of rings correlated to each anneal cycle at the bottoms of the holes. With regard to shape, holes formed on Si(5 5 12) have smooth edges and are circular, while those on Si(001) typically are not as circular. For both surface orientations, the holes oftentimes incorporate pits (5 @micron@ dia, 500-700 nm depth) or vertical structures (1 @micron@ dia, 150 nm height) at their centers. The conditions resulting in such structures, as well as their formation mechanism, are now under investigation. @FootnoteText@ This work is supported by the National Science Foundation.

SS-TuP11 The Structure of the (111) Surface of Bismuth*, **J. Sun**,* University of New Hampshire*; H. Mönig, J. Wells, P. Hofmann,* University of Aarhus, Denmark*; K. Pohl,* University of New Hampshire

Bismuth is a group V semimetal with a very low density of states at the Fermi level. However, a small distortion of its rhombohedral (A7) bulk structure would give a cubic lattice, which should be a good metal. In view of this close relation between structure and electronic structure it is not surprising that the surfaces of Bi are very different from the bulk material. They are good, two-dimensional metals with an electronic structure governed by spin-orbit coupling@footnote 1-3@. The changes in the geometric structure which lead to these interesting properties are totally unknown. We have studied the surface structure of clean Bi(111) and the mean-square displacement of the surface atoms by low energy electron diffraction (LEED). Experimental and theoretical diffraction intensities are analyzed for sample temperatures of 140, 171, 218, 268 and 313K. The optimization of the structural and nonstructural parameters is carried out by minimizing a R-factor with the quadratic tensor model algorithm. This results in an excellent agreement between the experimental and calculated data and R-factors of less than 0.1 are obtained. Moreover, the short termination of the bulk on the surface is confirmed. The temperature-dependent relaxations of the first layer distances and the atomic vibrations in the surface region are discussed. @FootnoteText@ @footnote 1@S. Agergaard, C. S@phi@ndergaard, H. Li, M. B. Nielsen, S. V. Hoffmann, Z. Li and Ph. Hofmann, New Journal of Physics 3, 15.1 (2001)@footnote 2@Ch. R. Ast and H. Höchst, Phys. Rev. Lett. 87, 177602 (2001)@footnote 3@Yu. M. Koroteev, G. Bihlmayer, J. E. Gayone, E. V. Chulkov, S. Blügel, P. M. Echenique, and Ph. Hofmann, cond-mat/0404461 .

SS-TuP12 Tunable Lattice Parameter of Ultrathin Bismuth Film*, **J.T. Sadowski**, Y. Fujikawa, T. Nagao, A. Al-Mahboob, T. Sakurai,* Tohoku University, Japan

The study of the structure and electronic properties of ultra-thin metal films on semiconductor surfaces has always attracted significant attention. To establish better control of the crystalline and electronic properties of the metallic layers, it is necessary to understand the factors governing their epitaxial growth, namely, surface free energies and stress relaxation effects. Semimetal bismuth (Bi) has distinctive electronic properties due to its covalent-like bonds and highly anisotropic Fermi surface. Moreover, results of our electron diffraction and scanning tunneling microscopy (STM) experiments show that Bi undergoes an allotropic transformation as a function of thickness on the scale of several layers, during the RT growth on Si(111)-7x7. After the initial formation of the Bi wetting layer, Bi grows with a new {012}-oriented phase, with a structure different from bulk Bi. With increasing the Bi coverage, above the critical thickness the film transforms into the bulk-like Bi(001) phase. Calculations suggest that the {012} phase with even-number layers is stabilized by forming a puckered-layer structure, which results in the formation of flat and well ordered film, reflecting the 2D structure of the {012} phase. Most interestingly, the lattice parameter of the Bi{012} phase can be tuned to a great extent by changing the nature and strength of the interactions between the Bi film and the substrate. Using the results of systematic diffraction and STM studies combined with the theoretical calculations, we will discuss the atomic structure of the Bi{012} film grown on the various surfaces (clean Si(111), H-Si(111), Bi and Au superstructures on Si(111)).

SS-TuP13 Stacking Fault Formation on Ir(111)*, **C. Busse**,* RWTH Aachen, Germany, Denmark*; C. Polop, T. Michely,* RWTH Aachen, Germany

The formation of stacking faults during homoepitaxial growth was observed in the model system Ir/Ir(111) (crystal structure: face-centered cubic) under a wide range of deposition parameters (sample temperature and deposition rate) using scanning tunneling microscopy (STM). A quantitative model can explain the observations and proves that stacking faults form out of small clusters that can occupy faulted hexagonal close-packed adsorption sites with significant probability in thermal equilibrium. Metastable areas in the wrong stacking sequence then grow out of these clusters by sufficiently fast addition of adatoms. This model is expected to hold for other systems as well. Upon further growth, islands in the same stacking coalesce, but islands in different stacking sequences do not. In the latter case, atoms can, however, move to the energetically favourable, regular stacking via a kink-flip process (self-healing). In the ideal case this leads to a complete disappearance of the wrong stacking and a defect-free film evolves. This effect can be observed in situ by annealing experiments.

SS-TuP14 Observation of Standing Waves in Si(111)@sr@3x@sr@3-Ag Islands at Room Temperature*, **T. Ishizuka**, H. Hirayama,* Tokyo Institute of Technology, Japan

It is widely accepted that Si(111)@sr@3x@sr@3-Ag surface has S1 surface state with a free electron like dispersion. The free-electron like surface dispersion has been confirmed by observing standing wave patterns at the @sr@3x@sr@3-Ag domain boundaries in STM at 5K [1]. In this study, we demonstrated that the free-electron like @sr@3x@sr@3-Ag surfaces can be utilized as the template for the nano-sized quantum structure construction. We obtained nano-scale @sr@3x@sr@3-Ag islands by depositing sub monolayer Ag on the Si(111)7x7 substrate surfaces at 770K. The standing wave patterns of electrons confined in the nano-islands were observed by a STM-based dI/dV mapping at 70K and room temperature. In the dI/dV images, the standing wave patterns were observed in the inside of the @sr@3x@sr@3-Ag islands of the size below 20nm. We found that the patterns persisted even at room temperature in the islands of 10nm scale. Then, we calculated the standing wave patterns numerically by solving Schrodinger equation for some islands with complex shapes using Finite Element Method(FEM). The numerical results reproduced characteristics of the observed standing wave patterns successfully, though the coincidence was not perfect. Furthermore, we fabricated point defects on @sr@3x@sr@3 Ag island artificially by using STM tip, and observed the resultant change of standing wave pattern. These results indicated that the 10nm scale islands still worked as Quantum Wells(QWs) even at room temperature. The shape of the islands could be modified by the STM tip induced atom manipulation. The confined electronic states are numerically predictable. These are preliminary demonstrations of the artificial design and fabrication of nano-sized QWs workable at room temperature on the template of the @sr@3x@sr@3-Ag surfaces.[1]N.Sato and S.Takeda PRB.59.3.2035(1999).

SS-TuP15 Electronic Structure of KDP and DKDP Nonlinear Optical Crystals Studied by Soft X-Ray Absorption and Emission Spectroscopies*, **S.O. Kucheyev**, C.F. Bostedt, T. van Buuren, T.M. Willey, S.G. Demos, T.A. Land, A.V. Hamza, T.E. Felter, L.J. Terminello, A.J. Nelson,* Lawrence Livermore National Laboratory

The surface and bulk electronic structure of KD@sub 2x@H@sub 2(1-x)@PO@sub 4@ single crystals, so-called KDP (x = 0) and DKDP (x > 0), with a deuteration degree x of 0.0, 0.3, and 0.6, is studied by soft x-ray absorption near-edge structure (XANES) and x-ray emission (XES) spectroscopies. High-resolution O K-edge, P L@sub 2,3@-edge, and K L@sub 2,3@-edge XANES and XES spectra reveal that the element-specific partial density of states in the conduction and valence bands is essentially independent of deuteration x. Projected densities of states in the conduction band also appear to be essentially identical for tetragonal and orthorhombic phases, consistent with previous band structure calculations. A decrease in sample temperature from 300 to 77 K results in an ~0.4 eV shift in the valence band edge (probed by XES), with negligible changes to the conduction band edge (probed by XANES) as the material transforms from the tetragonal to orthorhombic phase. We assign XANES and XES peaks based on previous molecular orbital and band-structure calculations. Results also show that high-intensity x-ray irradiation results in material decomposition into water and KPO@sub 3@ cyclo- and polyphosphates.

SS-TuP16 Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth*,* ***V.N. Antonov,*** *J.S. Palmer, P.S. Waggoner, A.S. Bhatti, J.H. Weaver,* University of Illinois at Urbana-Champaign

Physical vapor deposition onto rare gas buffer layers leads to the spontaneous formation of clusters. During the thermal desorption of the buffer, these clusters diffuse and aggregate into larger structures, a process known as buffer-layer-assisted growth and desorption assisted coalescence. We studied the effect of buffer thickness and the rate of buffer desorption on the extent of this aggregation for Ag, Au, Cu, Pd, Co, and Ni particles on a solid Xe surface. On the basis of these experiments, results from Monte Carlo simulations and the existing theoretical models for cluster-cluster aggregation, we report the Arrhenius parameters for nanoparticle slip-diffusion. The effective activation energies range from 0.12 for small Ag clusters (few hundred atoms) to 0.60 eV for ramified Ni islands (millions of atoms), and the giant pre-exponential factors were found to differ by many orders of magnitude. Significantly, the pre-exponential factors follow a Meyer-Neldel type dependence on the corresponding effective activation energy, with a characteristic Meyer-Neldel energy of 6.9 meV. This energy is associated with the phononic excitations in solid Xe that are responsible for nanostructure mobility. This dependence should be a characteristic feature of nanoparticle diffusion.

SS-TuP17 Epitaxial Cu Nanowire Arrays Grown on H-Si(110) using Glancing Angle Deposition*,* ***H. Alouach,*** *G.J. Mankey,* The University of Alabama

We report the growth of epitaxial nanowire arrays using the technique of glancing angle deposition with substrate rotation. Epitaxial copper nanowire arrays were deposited on H-terminated Si(110) using electron beam evaporation. The nanowire arrays were characterized with x-ray diffraction, atomic force microscopy and scanning electron microscopy. Individual nanowires were confirmed to be single crystal by examination with transmission electron microscopy. The epitaxial growth involves twin formation with the epitaxial orientation relationships: Cu(111)//Si(110) with Cu[1-10]//Si[001] and Cu[-110]//Si[001]. As the angle of incidence is increased, the Cu grows as isolated columns with a spacing that increases as the angle of incidence is increased. However, the thickness limit for epitaxial growth is reduced as the angle of incidence is increased, and it is approximately 300 nm for a deposition angle of 75°. The X-ray rocking curves for samples deposited at increasing polar angles show steadily improving crystal orientation up to a deposition angle of about 35°. Beyond 65° deposition angle, the rocking curves show split diffraction peaks indicating that there are two distinct orientations. In addition, the split peaks have a much lower FWHM. The observed behavior will be explained based on arguments involving unidirectional diffusion arising from adatom parallel momentum. This work was supported by the NSF.

SS-TuP18 Modification of Surface Electronic Structure Due to Scattering from a Quasi-Periodic Potential in Ag/GaAs(110)*,* ***D. Eom,*** *C.-S. Jiang, H.-B. Yu, Q. Niu,* University of Texas at Austin*; P. Ebert,* Institut für Festkörperforschung, Germany*; C.-K. Shih,* University of Texas at Austin

An extensive study has been done on the metal films grown on the semiconductor substrates because of their practical and scientific issues. One interesting system is the silver film deposited on the GaAs(110) surface using the so-called two-step process: If Ag is deposited on GaAs (110) surface at low temperature (~77K) and subsequently annealed to room temperature, then it will form an atomically flat film. A detailed morphology, however, looks more like an array of two stripes, one is thick and one is thin, whose sequence is quasi-periodic. By using this model system, we explore the effect of quasi-periodic potential on the surface states of the silver film using a low-temperature scanning tunneling microscope (LT-STM) operated at 5.5 K. Spatially resolved tunneling spectra are analyzed in reciprocal space (i.e. Fourier space). We found that such a quasi-periodically modulated potential leads to a very complicated electronic structures. Unlike the periodic potential that leads to energy gaps in the well-defined Brillouin zone boundary, the quasi-periodic potential results in a hierarchical structure of gaps in the k-space. Detailed analysis combining theory and experiment will be presented.

SS-TuP19 Structure and Thermal Stability of Thin Fe Films on Al(001) Surfaces with Ti Interlayers@footnote 1@*,* ***C.V. Ramana,*** Montana State University-Bozeman*; B.-S. Choi,* Jeonju University, South Korea*; R.J. Smith,* Montana State University-Bozeman

Thermal effects and chemical reactions can induce complex changes in the electrical and magnetic properties of thin metal film device structures. Achieving stability of these structures at elevated temperatures is therefore important to operation, and becomes more difficult as the film thickness is reduced to the nanometer regime. In the present work we investigate the structure of Fe films grown on the Al(001) surface with extremely thin Ti interlayers at the interface. Using Rutherford backscattering and channeling (RBS/c), we identify the bcc structure of the Fe(001) film, with the [100] axis rotated 45° relative to the [100] axis of the Al(100) substrate, and an interplanar distance of 1.44Å. RBS/c and low-energy ion scattering (LEIS) were then used to evaluate the thermal stability of the interface. The resulting epitaxial structure is observed to be stable for temperatures up to ~200°C, at which point the diffusion of Al towards the surface begins. At ~400°C, the sample structure begins to disorder. @FootnoteText@ @footnote 1@Work Supported by NSF Grant DMR-0077534.

SS-TuP20 XPS and AFM Study of K Promoted Supported Au Nanoclusters*,* *Y. Yang,* University of Calfornia, Santa Barbara*; M.M. Sushchikh,* ***S.A. Sardar,*** *E.W. McFarland,* University of California, Santa Barbara

It has been observed in high pressure reactors that K can increase the activity for CO oxidization of Au nanoclusters formed in block copolymer micelles and deposited on titania supports. UHV in situ characterization shows that the surface species, K@sub 3@ N and carbonates are discomposed after heating the surface to 800 K in UHV. K remains on the surface, however, the XPS signal from Au disappears during the heating process. Surprisingly, repeat XPS following exposure of the surface to air shows an observable Au signal. The appearance/disappearance of the Au XPS signal is reproduced by cyclically exposing the sample to the air then re-heating to 800 K in UHV. Sputtering the surface heated in UHV recovers the Au XPS signal. A K-shell model is proposed to explain the data with the formation of a K@sub 2@ CO@sub 3@ overlayer on the Au cluster during heating in UHV. The concentration ratio between Au and K is approximately1:1.

SS-TuP22 Formation and Characterization of Au Coatings Deposited by Pulsed Laser Deposition on Alumina Particles for Low Temperature Oxidation of CO*,* *C.E. Allmond, M.C. Raphulu,* ***J.T. Calla,*** *R.J. Davis, J.M. Fitz-Gerald,* University of Virginia

Laser induced atomic flux processing affects a wide range of existing and emerging products used in aircraft, cutting tools, lithium-ion rechargeable batteries, superconductors, pharmaceutical drug formulations that employ micron to submicron sized particulate precursors in their manufacturing process. By attaching atomic to nano-sized clusters either in discrete or continuous form on the surface of the core particles, i.e. nano-functionalization of the particulate surface, materials and products with significantly enhanced properties can be obtained. In this paper we present an alternative use for these materials in the area of Au catalysis. Bulk gold is considered the least reactive metal in heterogeneous catalysis due to repulsion between the orbitals of the adsorbate and gold's filled d states. Gold's catalytic potential is not realized until it is present as supported nanoparticles. Supported gold nanoparticles are recognized as active catalysts for a variety of reactions, such as oxidation, epoxidation of propene, hydrogenation, water gas shift, and NO reduction. Despite intense effort, the underlying principles and the degree of their contribution to the activity of gold catalysts are currently debated. Although not conclusive, several factors have been proposed to explain the high activity of gold nanoparticles. These factors can be generalized into three classifications; metal particle size, metal oxidation state, and synergy between the metal particle and the support.

SS-TuP23 The Development of Pd and Ag Nanoparticles with Pulsed Laser Deposition*, **C.E. Allmond**, J.M. Howe, V.P. Oleshko, J.M. Fitz-Gerald,* University of Virginia

Small particles in the 1-100 nm range often exhibit significant properties that are promising for various practical applications, such as catalysis, electronics, imaging systems, etc. Therefore, it is important to develop preparation methods that are simple, effective and flexible in controlling particle size distributions. The development of novel materials has grown considerably with the introduction of nanoscale processing. A wide range of synthetic approaches regarding the preparation of metal nanoparticles in various matrices and at the surfaces, including reduction, sol-gel precipitation, solvent evaporation of hydrophobic colloids, cross-linking in colloidal aggregates, templates-directed methods, and biopolymer superstructures, has been reported. As an alternative, pulsed laser deposition is a novel preparation method. Palladium and silver nanoparticles, with sizes ranging from 1-10 nm, were deposited onto transmission electron microscope grids using pulsed laser deposition. Analysis of these nanoparticles incorporated high-resolution transmission electron microscopy, electron energy loss spectroscopy (EELS), and electron dispersion spectroscopy (EDS). The rationale behind this is two-fold: (1) is to obtain mean particle size and crystal structure as a function of fluence, gas pressure, and gas type and (2) is to establish parameters for site-specific catalysts.

SS-TuP24 Characterization of the Near-surface Structure, Composition and Surface Chemistry of Ultrathin Au Films on Pd{111}*, **T.G. Owens**, C.J. Baddeley, T.E. Jones,* University of St. Andrews, UK*; T.C.Q. Noakes, P. Bailey,* CCLRC Daresbury Laboratory, UK

There are many examples where bimetallic catalysts are known to outperform their monometallic counterparts. The synthesis of vinyl acetate monomer (VAM) from acetic acid and ethylene by Pd/Au catalysts is one such example exploited commercially by BP. In order to gain a fundamental understanding of the catalytic role of Au, we are interested in how the chemistry of Pd/Au bimetallic surfaces is influenced by surface structure and composition. Previous studies of the Pd{111}/Au system have reported that the first Au monolayer grows psuedomorphically on Pd{111} at 300 K while subsequent growth consists of films possessing a more Au-like structure, i.e. classic Stranski Krastanov growth. Medium Energy Ion Scattering (MEIS) has a unique ability to probe structure and composition of crystalline surfaces as a function of depth with monolayer resolution. In parallel with Scanning Tunnelling Microscopy (STM) measurements, we reveal that Au growth is more complex than previously assumed and identify an interfacial alloy structure with a quite different structure to either Au or Pd. In addition, we report the behaviour of ultrathin Au films as a function of pre-annealing treatment and we probe how the structure and composition of the near surface region is influenced by the adsorption of simple probe molecules.

SS-TuP25 Highly Stable Variable Temperature STM for Atomically and Time Resolved Imaging: The Dynamics of Self-Assembly at Surfaces*, **B. Diaconescu**, G. Nenchev, K. Pohl,* University of New Hampshire

Self-ordering growth of nanoarrays on strained interfaces is an attractive option for preparing highly ordered nano-templates of specific feature size densities. High-tech methods used for reducing of the feature sizes may thus be supplanted by this simple and elegant patterning technique. Reconstructed surfaces, e.g. Au(111) or Pt(111), and monolayer thick strained films, e.g. Ag or Cu on Ru(0001), exhibit well-ordered networks of misfit dislocations. These networks can serve as templates for the growth of mesoscopic-scale structures of large-scale order and size uniformity. The combination of interfacial stress and corrosion creates self-ordering arrays of unprecedented regularity. The great potential of this natural templating approach is that the feature sizes and densities are predicted to depend on the interfacial stress in these strained layers. We have the unique capability of being able to measure the resulting driving forces of self-assembly directly through time-resolved scanning tunneling microscopy. This enables us to determine the stability and elastic constants of 2D nano-templates@footnote 1@. For this purpose we designed and build a highly stable VT-STM@footnote 2@. It allows us to study the dynamics of self-assembly at strained metallic interfaces at the atomic scale in the temperature range 80-400K. An overview of the instrumental setup and it's performance will be given by variable temperature studies of self-organisation of nanostructures on Au(111) and Ag, and Cu films on Ru(0001) at different thicknesess. @FootnoteText@ @footnote 1@ K.Pohl et al. Nature 397,238 (1999)@footnote 2@ Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

SS-TuP26 Preparation and Chemical Oxidation Kinetics of Microcrystalline Tungsten Bronze Thin Films*, **E.B. Kadossov**, P. Rajasekar, N.F. Materer,* Oklahoma State University

Microcrystalline tungsten bronze (H@sub x@WO@sub 3@) thin films are prepared using wet chemical techniques or atomic hydrogen to reduce a tungsten oxide thin film. The oxide film is prepared by thermal oxidation of sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films is determined by X-ray diffraction. X-ray photoelectron and ultra-violet photoelectron spectroscopy show that these films are indistinguishable from conventionally prepared tungsten bronze powders. The quartz support allows the total amount of incorporated hydrogen in the film to be quantified by monitoring the absorbance at 900 nm. This technique is utilized to study the oxidation kinetics of these films by either oxygen gas or hydrogen peroxide aqueous solution. The resulting decay of the 900 nm absorbance intensity with time can be satisfactory fit to a kinetic model composed of two elementary steps. First, a proton must diffuse from the bulk to the surface. Next, a chemical reaction between the surface proton and the oxidant must occur. Conditions are such that the surface concentration of the oxidant adsorbed on the surface is effectively constant. In addition, this model implicitly assumes that the electron transfer step required for reduction of the oxidant is not rate limiting. From this kinetic model, both the proton diffusion coefficient and the surface activation energies can be estimated. The results are compared with previous nuclear magnetic resonances studies and electrochemical measurements.

SS-TuP27 Growth Studies of Thin Pt Films on the Cu(100) Surface by CAICISS, LEED and XPS*, **M. Walker**, C.R. Parkinson,* University of Warwick, UK*; C.F. McConville,* University of Warwick, UK, United Kingdom

The formation of a surface alloy upon room temperature deposition of Pt on the Cu(100) surface is observed by co-axial impact collission ion scattering spectrscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Simulations of the CAICISS results are given to support the proposed alloy structures from Pt coverages of 0.25 ML upwards, with comparisons between layer-by-layer, alloy and Pt surface cluster models. With increasing Pt coverage the surface region becomes Pt rich, with a small Pt overlayer observed at a Pt coverage of 2.35 ML and above. This indicates the onset of layer-by-layer growth of a pure Pt film. LEED observations indicate that this film is disordered. The effects of annealing at temperatures up to 600 °C are also shown for samples with Pt coverages of 0.25 ML and 2.75 ML. CAICISS and XPS clearly demonstrate the penetration of Pt in to the Cu substrate upon annealing. For Pt coverages greater than 2.35 ML, annealing at 300 °C causes Pt to penetrate down to the fourth and fifth layers of the substrate, forming a CuPt surface layer and Cu@sub2@Pt sub-surface layers. For Pt coverages of ~ 0.25 ML, annealing at 200 °C resulted in a small amount of Pt migrating towards the bulk. After annealing at 300 °C the sample contained approximately 7% Pt in each of the top three layers of the sample and small Pt concentrations in the fourth and fifth layers. Annealing at 600 °C results in the onset of significant migration in to the substrate in both cases.

SS-TuP28 NO Decomposition over K-Deposited Pd(111)*, **I. Nakamura**, H. Hamada, T. Fujitani,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

The adsorption and thermal reaction properties of NO on a K-deposited Pd(111) surface were investigated using infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption. For the K-deposited Pd(111) surface, two different NO adsorption sites were observed in addition to the Pd site. On the clean Pd(111) surface, the adsorption of NO was purely molecular and reversible, but on the K-deposited surface, the adsorbed NO decomposed to N@sub 2@ at two different temperatures, 530 and 610 K. The N@sub 2@ desorption at 530 K was due to the dissociation of NO, indicating that the NO dissociation sites were created on the Pd(111) surface by the deposition of K. On the other hand, the N@sub 2@ desorption at 610 K was due to the decomposition of NO@sub 2@, which was formed by the reaction of adsorbed NO with oxygen produced by NO dissociation. It was clearly shown that two active sites for the decomposition of NO to N@sub 2@ were newly created on the K-deposited Pd(111) surface.

SS-TuP31 Charge Exchange between Alkali Ions and Cerium Oxide Surfaces*, **G. Liu**, J. Yarmoff,* University of California, Riverside

CeO@sub 2@ has interesting catalytic properties, which are presumably the result of an electronic configuration that includes many valence electrons. Earlier, we showed that the probability for neutralization of low energy alkali ions scattered from metal surfaces is determined by resonant charge transfer (RCT) along the exit trajectory, and it depends on the local electrostatic potential (LEP) a few Å's above the scattering site.@footnote 1@ We also showed that RCT is effected by localized confined states in nanomaterials.@footnote 2@ The present work investigates the charge exchange between alkali ions and cerium oxide surfaces. The neutral fractions of 3 keV @super 23@Na@super +@ ions singly scattered from the Ce sites on CeO@sub 2@ single crystal surfaces were measured with time-of-flight spectroscopy. The angular dependence of the neutralization was found to be isotropic for CeO@sub 2@(111), while for CeO@sub 2@(100) the neutralization decreases for more grazing angles. The results from either surfaces cannot be explained by simple RCT theory, which predicts increased neutralization at grazing angles, and may therefore suggest that a new mechanism for charge transfer is operative with these materials. In order to ascertain the influence of the work function on ion neutralization, Cs and Br were deposited onto the CeO@sub 2@ surfaces to controllably decrease and increase the work function, respectively. Results for scattering from CeO@sub 2@(100) and CeO@sub 2@(111) will be compared and contrasted. @FootnoteText@ @footnote 1@C. B. Weare and J. A. Yarmoff, Surf. Sci. 348 (1996) 359.@footnote 2@G. F. Liu, Z. Sroubek and J. A. Yarmoff, Phys. Rev. Lett., in press. .

SS-TuP32 Inelastic Energy Losses and Ion Yields of Low Energy Ar@super +@ and Ne@super +@ from Transition Metals*, **A. Kutana**,* *K.P. Giapis,* California Institute of Technology

Inelastic losses and relative ion yields of 100-1300 eV Ar@super +@ and Ne@super +@ ions reflected off polycrystalline V, Nb, Ta, Zr, and Y surfaces were measured using a low energy scattering beamline apparatus. Use of a floating ICP source coupled to a small beam accelerator had overcome many problems pertinent to conventional sources in the sub-keV energy range and allowed measuring scattering energies with much greater precision. From the acquired energy spectra, peak positions of singly scattered ions were plotted versus the primary beam energy E@sub 0@ and compared with energies of totally elastic single collisions. For energies above 100 eV, the inelastic losses of singly scattered ions can be described by the power law E@sub 0@@super a@ with a<1. Scattering simulations based on the binary collision approximation with added local and nonlocal inelastic losses yielded the theoretical loss values that were related with the ones observed in experiment. For a given primary ion, the relative ion yields were generally found to vary insignificantly from one metal to another, except for the Ne@super +@-Y pair, where a much more efficient neutralization of Ne@super +@ was observed. Characteristic neutralization velocities were also estimated for the above projectile-target combinations.

SS-TuP33 Epitaxial Iron Oxide Growth on Vicinal Pt(111): Well-defined Defective Model Systems?*, **G. Ketteler**,* Lawrence Berkeley National Laboratory, University of California*; W. Ranke,* Fritz-Haber-Institute of the MPG, Germany

Heterogeneous catalysts consist often of metals in contact with oxides and the activity depends on the interaction between them. In addition, the defect structure of the surface is of high importance for the catalytic activity. The common electron-based surface science techniques allow the characterization of model catalyst surfaces with atomic precision. Studied model catalyst systems include single crystal surfaces, epitaxial compound films, or well-defined particles deposited on single-crystalline supports. However, real catalysts contain a defect structure which is difficult to model in a well-defined manner. In order to study the controlled introduction of defects into iron oxide model catalysts for the dehydrogenation of ethylbenzene to styrene, we have grown different iron oxide phases on a stepped Pt(9 11 11) single crystal surface and characterized the film structures by STM and high-resolution SPA-LEED measurements. The hope was that this may provide a way to introduce well-defined step defects into the epitaxially grown films. For coverages below 1 ML, FeO(111) films wet the vicinal Pt substrate. The step structure changes under formation of doubled and triplicated terrace widths and step heights. Further cycles of iron deposition and oxidation lead to a Stranski-Krastanov-type growth of Fe@sub 3@O@sub 4@(111) islands which initially are elongated along the edge direction. However, the morphology of a coalesced closed film is almost unaffected by the underlying substrate step morphology. High pressure oxidation of Fe@sub 3@O@sub 4@ films results in poorly defined Fe@sub 2@O@sub 3@(0001). Although FeO films grown on the vicinal Pt surface may serve as model systems for systematic studies of well-defined defective oxide surfaces, the catalytically more relevant Fe@sub 3@O@sub 4@ and Fe@sub 2@O@sub 3@ phases could not be obtained reproducibly with a well-defined defect structure.

SS-TuP34 Anomalous Diffusion Permeability of an Interphase Interface in Mo-Ni System Under High-Energy Electron Irradiation*, **G.G. Bondarenko**, M.M. Yakunkim, A.V. Artamonov,* Moscow Institute of Electronics and Mathematics (Technical University), Moscow, Russia*; S.P. Ostashkin,* Russian State University of Innovational Technologies and Management, Moscow, Russia

Some of the problems of the theory of transport in solids are anomalous atomic mobility and deviations from the equilibrium concentrations at an interphase interface caused by high-energy irradiation. The problem of anomalous mass transfer of components during long-term electron irradiation can be solved using information on phase diagrams. We study the Mo-Ni system during electron irradiation over the time it takes for stationary state to be achieved and compare the states obtained with equilibrium states. Samples in form of two-layer plates 0.05 (Mo) and 1.5 mm (Ni) in thickness were irradiated in a linear electron accelerator at energies of E = 2-8 MeV in steps of 2 MeV for the time it took for equilibrium structures to be formed. Irradiation was carried out in a special temperature-controlled chamber at 1000 K. The isothermal section of this system at E = 0 was preliminary obtained. Isothermal sections of the phase diagram at various values of E were constructed from the data of phase analysis. We found that the quasi-equilibrium irradiated diffusion zone at the interface is a nanoregion ~20 nm in size. The concentrations of components at the interphase interface significantly change during irradiation. As a result of electron irradiation, the maximum nickel content in the @delta@-phase increases by 12%, the nickel concentration in the molybdenum-based solid solution at the interface increases by a factor of almost four and is equal to ~10% at E = 8 MeV. Changes in the component concentrations at interphase interfaces can be described without applying thermodynamics by introducing the concept of the diffusion permeability of an interphase interface. Given the appearance of a phase diagram at various values of E, it is possible to calculate the diffusion permeability of the interface for all cases. This approach was used to account for the concentration deviations detected at the interphase interface during high-energy electron irradiation.

SS-TuP35 Structure Transformation of Palladium and Iridium Clusters on the W (110) Surfaces at Initial Stage*, **T.-Y. Fu**,* National Taiwan Normal University, Taiwan, ROC*; Y.-H. Wang,* National Taiwan Normal University, Taiwan, Taiwan R.O.C.*; T.T. Tsong,* Institute of Physics, Taiwan

The initial stages of cluster nucleation of Pd or Ir adatoms on W (110) surfaces and in the vicinity of surface steps are observed directly by a field ion microscope (FIM). At the beginning, the most stable structures of Pd and Ir clusters are both linear chains, which are parallel to the nearest-neighbor stacking directions of the substrate. Different to the Pd clusters which the preferred structure is a 2-D compact island when the chain length is beyond 8 atoms, the linear Ir chains are apparently more stable and the greater coverage and higher temperature are necessary conditions for 1-D to 2-D transition. Both of Pd and Ir 2-D islands are pseudomorphic structure. As the number of Pd adatoms increasing to approximate monolayer coverage, the structures of clusters transfer to three-dimensional island. The structure transition from bcc (110) to fcc (111) of 3-D Pd clusters is shown. The quit complex transform behaviors of Ir clusters are also discussed.

SS-TuP36 Adsorption and Reaction of Oxygen and Hydrogen on Free Platinum Clusters*, **M. Andersson**, A. Rosen,* Chalmers University of Technology and Goteborg University, Sweden

In a cluster beam experiment metal clusters are produced with a pulsed laser vaporization source, kept at room temperature or liquid nitrogen temperature. The beam of neutral clusters passes two low-pressure collision cells and clusters and reaction products are detected with laser ionization and time-of-flight mass spectrometry. Thus, the reaction probability in a cluster-molecule collision can be determined.@footnote 1@ Stable reaction products with O@sub 2@ are detected for clusters with more than 6 atoms, and a high and relatively size-independent reaction probability of about 0.3 is measured. Also H@sub 2@ adsorbs readily on Pt@sub n@ but the exact number of adsorbed molecules is difficult to determine because of the Pt isotope distribution. If the clusters first react with O@sub 2@ and then with H@sub 2@ one can observe that the reaction of Pt@sub n@(O@sub 2@)@sub m@ with H@sub 2@ results in the removal of oxygen atoms from the cluster. This is interpreted as formation of water molecules, which subsequently desorb. The efficiency of the catalytic water formation is high on all cluster sizes measured (7-30 atoms), with only a weak dependence on cluster size.@footnote 2@ The configuration with two separate reaction cells enables reversing the order of interaction with the reactant molecules, and a high reaction efficiency is measured also when the Pt clusters first interact with H@sub 2@. @FootnoteText@ @footnote 1@ M. Andersson, J.L. Persson, and A. Rosen, J. Phys. Chem. 100, 12222 (1996).@footnote 2@ M. Andersson and A. Rosen, J. Chem. Phys. 117, 7051 (2002). .

SS-TuP37 Preperation of Ultra-thin Lattice Matched Multilayers of Cr@sub 0.63@Mo@sub0.37@ and MgO*, K.B. Gylfason,* Biopharmaceuticals, Iceland*; S. Olafsson, I. Meyvantsson,* University of Iceland, Iceland*; K. Johnsen,* Biopharmaceuticals, Iceland*; **J.T. Gudmundsson,*** University of Iceland, Iceland

We report on the preparation of a lattice matched hetheroepitaxial system in a magnetron sputtering discharge. Cr@sub 0.63@Mo@sub0.37@ thin films were grown on MgO(1 0 0) using a DC discharge, and an MgO overlayer was grown on top by reactive sputtering in a pulsed bipolar discharge. The composition of the binary metal alloy is chosen so that the film is lattice matched to the substrate when the direction of the film is parallel to the direction of the substrate. Ex situ X-ray diffraction (XRD) and low angle X-ray reflectivity measurements were performed to determine the film structure, film thickness, as well as the surface and interface roughness. The minimum thickness for continuity of the binary metal alloy film was determined using four point probe resistance measurements. The insulating properties of the MgO film as a function of thickness were assessed by measuring the tunnelling current I-V characteristics of a metal-insulator-metal structure.

SS-TuP39 O2-covered Reduced TiO2(110) Rutile: Dynamics and Chemistry*, **Y. Wang**, G.S. Hwang,* The University of Texas at Austin

The rutile TiO2(110) surface has been widely used as a catalyst for photochemical reactions and a support for transition metal catalysts. Molecular O2 adsorption plays an important role in determining the activity of TiO2 and supported metal catalysts. Surface bound oxygen species may directly influence chemical and photochemical processes occurring on TiO2. In addition, O2 exposure leads to significant structural changes of supported metal particles, which may in turn affect their catalytic activity. It has been found that molecular O2 adsorbs on TiO2(110) only when O-vacancies are present. Despite its importance, however the exact chemistry and dynamics of adsorbed O2 molecules on reduced TiO2(110) are still unclear. Using density functional theory calculations, we have investigated the adsorption and diffusion of oxygen species on the reduced TiO2 (110) surface. We have found that molecular O2 strongly binds not only to O-vacancies, but also to Ti(5c) neighbors, due to delocalization of unpaired electrons arising from removal of neutral bridging oxygen. Our results show that molecular O2 can jump across an oxygen vacancy and diffuse along a Ti(5c) row with moderate barriers. On the other hand, atomic O diffusion along a Ti(5c) row is rather unlikely at low temperatures (< 300K), because of the relatively higher probability of O-O formation by interaction with an adjacent bridging O(2c) atom. Based on our calculation results, we will discuss the diffusion and healing of O vacancies associated with O2 adsorption. We will also present the structure and energetics of higher coverage O2 adsorption and the chemistry of O2-covered reduced TiO2(110) surfaces.

SS-TuP40 Growth and Reactivity of Pt, Rh and Pt-Rh Nanoparticles on TiO@sub 2@(110)*, **S. Ma**, J.S. Ratliff, D.A. Chen,* University of South Carolina

Pt, Rh and Pt-Rh nanoparticles have been deposited on TiO@sub 2@(110) at room temperature and have been characterized by scanning tunneling microscopy (STM). The deposition of a small amount of Pt on the surface (0.12 ML) results in particles with an average diameter of 22.7+4.2 Å and height of 4.4+1.2 Å. In contrast to the growth of Cu and Ni on TiO@sub 2@(110), the Pt particles do not exhibit a preference to reside at the step edges. At higher Pt coverages (2 ML), the average size of the particles increases to 30.4+4.6 Å in diameter and 8.5+2.0 Å in height. Larger particles with roughly the same size distribution could be produced by depositing at room temperature and annealing to elevated temperatures. For example, after annealing the 2 ML coverage of Pt to 500 K, particles sizes ranged from 40-45 Å in diameter and ~10 Å in height. Further heating to 700 K increased the sizes of the particles to ~50 Å in diameter and 10-12 Å in height, and the largest particles were prepared by annealing at 1000 K (60 Å in diameter, 15 Å in height). Since Pt particles on TiO@sub 2@ are known to encapsulate with a TiO@sub x@ species upon annealing, X-ray photoelectron studies were carried out on the Pt particles annealed to 1000 K. However, there was no evidence for Ti@super +4@ reduction or Pt oxidation in the Ti(2p) and Pt(4f) regions. Possible encapsulation of the nanoparticles by TiO@sub x@ will be further studied by low energy ion scattering as well as grazing angle X-ray photoelectron spectroscopy experiments. The reduction of NO by CO on the monometallic and bimetallic clusters of different sizes will be investigated by temperature programmed desorption.

SS-TuP41 Adsorption of L-phenylglycine on Anatase TiO@sub2@(101) and (001): A NEXAFS and Photoemission Study*, **A.G. Thomas,*** University of Manchester, UK, U.K.*; C. Chatwin, W.R. Flavell, D. Tsoutsou,* University of Manchester, UK*; T. Johal, J. Purton,* CCLRC Daresbury Laboratory, UK

We present a study of the adsorption of L-phenylglycine from submonolayer to multilayer coverage on the (101)(1x1) surface of anatase phase TiO@sub2@. Photoemission is used to determine changes to the electronic structure of the substrate and adsorbate and the NEXAFS searchlight effect is used to determine the orientation of the phenylglycine on the substrate. NEXAFS spectra recorded from multilayers adsorbed from the vacuum show good agreement with solvent deposited thick films of glycine and phenylalanine@footnote 1@. From the intensity dependence of the ring @pi@* resonance on photon incidence angle in NEXAFS it appears that the molecule forms a disordered layer at all coverages studied here. Furthermore, again at all coverages studied, it appears that N is being lost from the amino acid molecule with time through a photon induced process. A similar result has been observed when glycine adsorbed on the rutile TiO@sub2@ (110)(1x2) surface is subjected to photons of energy 55 eV@footnote 2@. @FootnoteText@ @footnote 1@ J. Boese, A. Osanna, C. Jacobsen, J.Kirz. J. Electron Spectroscopy and Relat. Phenom. 85 (1997) 9.@footnote 2@ E. Soria, I. Colera, E. Roman, E.M. Williams, J.L. De Segovia. Surface Science 451 (2000) 188.

SS-TuP42 Deconvolution of the Fuchs-Kliewer Phonon Spectrum of Co@sub 3@O@sub 4@(110) Single Crystal Surfaces*, **E.M. Malone**, S.C. Petitto, M.A. Langell,* University of Nebraska-Lincoln

The Fuchs-Kliewer phonon spectrum of single crystal Co@sub 3@O@sub 4@(110) has been treated with a Fourier transform log deconvolution method which removes multiple scattering features from the single loss spectrum. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) first characterized the Co@sub 3@O@sub 4@ crystal establishing the cleanliness, composition, and order of the (110) surface. High resolution electron energy loss spectroscopy (HREELS) was then used to obtain the phonon spectrum over the incident electron energy range of 2.25 to 14.25 eV. Due to the strong dipole cross section for the Fuchs-Kliewer phonon modes, intense multiple electron scattering was detected, which provided a complicated and overlapping combination of all possible loss modes. Deconvolution removed the multiple loss modes to produce well-resolved Fuchs-Kliewer fundamental phonon losses at 26.8, 47.5, 71.1 and 84.7 meV (216, 383, 573 and 683 cm-1). The series of multiple loss peaks were also identified using standard peak fitting procedures, which also confirmed the single loss energies obtained with the deconvolution procedure.

SS-TuP43 Kinetic Energy Dependent Oxidation Processes on Copper Surfaces*, **K. Moritani,*** Japan Atomic Energy Research Institute, Japan*; M. Okada,* Osaka University, Japan*; A. Yoshigoe, Y. Teraoka,* Japan Atomic Energy Research Institute, Japan*; T. Kasai,* Osaka University, Japan

The oxidation of Cu has been of great interest because of the important role of Cu oxides in material science, for example, high Tc superconductors of cuprates and solar cells. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes have been little elucidated from kinetics and dynamics points of view. In the present work, we studied the oxidation of Cu surfaces with a hyperthermal O@sub 2@ molecular beam (HOMB) using high-resolution X-ray photoemission spectroscopy (XPS) in conjunction with a synchrotron radiation (SR) source. All experiments were performed with the surface reaction analysis apparatus (SUREAC 2000) constructed in BL23SU at SPring-8. The kinetic energy of incident O@sub 2@ can be controlled by changing the O@sub 2@, He and/or Ar gas mixing ratios and the nozzle temperature. The incident direction of the HOMB is along the surface normal of the sample. The surface temperature was kept at 300 K. After the irradiation of a proper amount of HOMB, high-resolution XPS spectra were measured at ~300 K using SR. We measured O-uptake curves, determined from the integration of O-1s XPS on the Cu(111), (100) and (110) surfaces spectra, after the HOMB irradiation and the exposure to the oxygen atmosphere. The kinetic energy of HOMB varied from 0.1 to 2.3 eV. The oxidation under 0.3 ML on the Cu(111) proceeded efficiently even with the ambient thermal O@sub 2@ gas, while further oxidation required the higher kinetic energy of O@sub 2@ molecules. The oxide structure above 0.3 ML changed to be a distorted Cu(100)-(@sr@2X@sr@2)R45°-O layer on the Cu(111). This reconstruction is induced by the additional incident energy. We will compare the data on Cu(111), (100) and (110) surfaces and discuss possible models of oxidation processes of Cu on the basis of the incident-energy dependence of the O-uptake curve.

SS-TuP44 The Adsorption of Benzene on Oxide Surfaces*, **M.-S. Chen**, A.K. Santra, D.W. Goodman,* Texas A&M University

The orientation and growth of benzene on various well-ordered oxide surfaces have been investigated with high resolution electron energy loss spectroscopy (HREELS), Auger spectroscopy (AES) and low-energy electron diffraction (LEED). Benzene on the Mo(112)-c(2x2)-[SiO4] surface is bound with its molecular plane parallel to the surface plane at submonolayer coverages. At intermediate coverages (1-3 ML), in contrast to benzene adsorption on metal surfaces, a layer-by-layer growth model where the benzene molecules bond parallel to the surface is observed. This is the first reported observation of benzene multilayer growth where the benzene molecules remain exclusively in a configuration parallel to the surface plane. In contrast, on SiO2 and TiOx thin films grown on the Mo(112), a tilted adsorption geometry with layer-by-layer grew up to 5-6 ML was found with a crystalline phase occurring at higher coverages. On a TiOx-SiO2 surface, where both parallel and tilted-up geometries coexist, crystalline benzene clusters formed at the second layer.

SS-TuP45 Competing Kinetic and Energetic Effects in the Adsorption of Ortho- and Para-H@sub 2@ on NaCl(001)*, J.P. Toennies,* Max-Planck-Institute für Strömungsforschung, Germany*; **F. Traeger**,* Ruhr-Universität Bochum and MPISF Göttingen, Germany*; C. Wöll,* Ruhr-Universität Bochum, Germany

Due to the electrostatic interaction of the hydrogen molecule's quadrupole moment with the electric field of the surface the ortho and para modifications experience slightly different molecule-surface potentials, which has been verified by scattering of n- and p-H@sub 2@ beams from the clean NaCl surface. A complementary way to study the molecule-surface interaction is to investigate the (1x1) monolayers of n-H@sub 2@ and p-H@sub 2@ on NaCl at 8 K with elastic and inelastic He atom scattering. The ortho-para differences result in 10-12 % higher frequencies for the external vibrations of o-H@sub 2@. Therefore, the relative intensities of the peaks in time-of-flight spectra of the scattered He atom provide information on the composition of the layer. Under steady-state conditions at H@sub 2@ gas pressures between 2.5 x 10@super -8@ mbar and 9.3 x 10@super -7@ mbar as well as during the desorption of the layer without gas pressure time-of-flight spectra have been recorded and are compared to desorption curves, i.e. the specular He intensity during desorption. Conflicting evidence regarding the adsorption probability for ortho- and para-H@sub 2@ is found, which is only partly in agreement with a model of thermodynamically and kinetically controlled adsorption proposed by Heidberg et al. from IR spectroscopy.

SS-TuP46 First Stages of Water Absorption on Alkali Halides Surfaces Studied by Scanning Polarization Force Microscopy*, **A. Verdaguer**, G.M. Sacha, M. Salmeron,* Lawrence Berkeley National Laboratory

Adsorption of water on sodium chlorite has been studied using scanning polarization force microscopy. A crystal is cleaved at low humidity (10% RH) and then humidity is increased as topography, contact potential and mobility of the ions is measured. At a critical humidity (40% for NaCl) important changes in the surface potential and ionic mobility occurred. Topographical changes occurred as well, in the form of step motion. We focused our study on the changes on the surface immediately before this critical humidity is reached. The evolution in the topographical and electrical properties and the ion mobility on the steps and the terraces as we approach to that point has been studied. An increase in the topographic contrast on the steps appears as we approach to the critical humidity. The increase in topographic electrostatic contrast is due to an increase in ionic mobility at step, indicative of ionic dissolution. As the mobility increases the difference between the local potential at the steps and on the terraces, measured from the Kelvin Probe signal, decreases. This supports the model deduced from the topography and indicates that the initial potential at the steps disappears due to the increased ionic mobility. The data obtained suggest us a model for the first stages of the dissolution of the crystal.

SS-TuP47 XPS and XAS Study of Water and Atomic Oxygen Co-absorbed on Pt(111)*, **L.-A. Naslund**, K. Andersson, T. Schiros,* Stockholm University, Sweden*; H. Ogasawara, A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On hexagonal metal surfaces, like Pt(111), water molecules adsorb intact with strong intermolecular forces between the water molecules. A combined X-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) study shows that water (D@sub 2@O) co-adsorbed with atomic oxygen on Pt(111) stimulate dissociation of the water molecule and form a saturated hydrogen bonded network of OD and D@sub 2@O in the surface plane. The interaction with the Pt(111) surface is strong and give rise to a chemical shift of the Pt 4f orbital that is different from the results for water on Pt(111). XAS with polarized light shows that OD is standing up while D@sub 2@O is laying down. The amount of OD and D@sub 2@O are 0.28 ML and 0.55 ML, respectively, which gives an OD/D@sub 2@O ratio of 2. Upon heating D@sub 2@O desorbs and a reversible process gives back atomic oxygen.

SS-TuP48 XPS Study of Water on Cu(110)*, K. Andersson, A. Gomez,* Stockholm University, Sweden*; C. Glover,* MAXLab Lund University, Sweden*; L.G.M. Pettersson,* Stockholm University, Sweden*; **A. Nilsson**, H. Ogasawara,* Stanford University

The chemical interaction between water and a metal surface is important in many practical fields,including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On smooth metal surfaces, (e.g. fcc(111)), water molecules adsorb intact with strong intermolecular forces between the water molecules. This leads to the formation of a hexagonal two-dimensional ice lattice proposed as a "bilayer structure". The unit cell contains two water molecules, which are different in the interaction with respect to the metal surface. On the other hand, less is known about the behaviour of water on atomically rough surfaces (e.g. fcc(110)). An x-ray photoelectron spectroscopic (XPS) study was undertaken of the water/Cu(110)-system and we find that water adsorbs non-dissociatively on Cu(110) at temperatures below 165 K in contrast to a previous XPS study@footnote 1@. Above 165 K we find partial dissociation to take place. @FootnoteText@ @footnote 1@ Ch. Ammon, A. Bayer, H.-P. Steinruck and G. Held, Chem. Phys. Lett. 377 (2003) 163â?"169.

SS-TuP49 Water Dissociation on Ru(001): An Activated Process*, **H. Ogasawara**,* Stanford Synchrotron Radiation Laboratory*; K. Andersson,* Stanford Synchrotron Radiation Laboratory, Stockholm University, Sweden*; T. Schiros,* Stockholm University, Sweden*; A. Nikitin,* Stanford University*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On Pt(111), it was shown that in the first layer all the molecules bind directly to the surface and to each other through the in-layer H-bonds without dissociation, creating a nearly flat overlayer. The water molecules are adsorbed through alternating metal-oxygen (M-O) and metal-hydrogen (M-HO) bonds@footnote 1@. On Ru(001), the water layer on Ru(001) shares similarities with the first water layer on Pt(111). We, however, obtained a dissociated state by irradiation of the adsorbed film by x-rays or heating the surface in water vapor above the desorption temperature. The latter shows a clear isotope effect between H20 and D2O indicating an activated dissociation process with a barrier slightly larger than the desorption channel. Previous theoretical and experimental disagreements can be explained in terms of electron or x-ray beam induced dissociation and under estimation of the dissociation barrier. We will also discuss about the bonding mechanism of water on Ru(001) based on DFT calculation. @FootnoteText@ @footnote 1@ H. Ogasawara et al, Phys. Rev. Lett. 89 (2002). .

SS-TuP50 Investigation of OH Desorption Energies and Reaction Paths within the H2/O2 Reaction on a Pd Catalyst using Kinetic Modelling and Laser-induced Fluorescence*, J.C.G. Andrae,* Royal Institute of Technology, Sweden*; A. Johansson,* Goteborg University and Chalmers, Sweden*; **P. Bjornbom**,* Royal Institute of Technology, Sweden*; A. Rosen,* Goteborg University and Chalmers, Sweden

A kinetic model for the H@sub 2@/O@sub 2@ reaction on a polycrystalline palladium catalyst has been constructed from experimental data. The aim was to obtain a deeper understand of the coverage-dependent OH desorption energy. The CHEMKIN software package was used in the modelling and each adsorbed oxygen atom was set to cover four Pd surface sites. The yield of OH and the water production were measured with laser-induced fluorescence (LIF) and microcalorimetry as a function of the relative hydrogen concentration, @alpha@@sub H2@. The temperature of the catalyst was 1300 K, the total pressure was 13 Pa and the flow was set to 100 SCCM. In fitting the model to the experimental data, the OH desorption energy E@super d@@sub OH@ was found to have a first-order coverage dependence according to: E@super d@@sub OH@ (@theta@)= E@super d@@sub OH@(0)-B@theta@, where @theta@ is the total coverage and B is a constant set to 92 kJ/mol. The desorption energy at zero coverage E@super d@@sub OH@(0) was determined to be 226 kJ/mol. The model could qualitatively and quantitatively reproduce the OH apparent desorption energy as a function of @alpha@@sub H2@ therefore it is believed that the coverage could be predicted by the model. It was found that the coverage on the Pd surface is in principle dominated by oxygen for all @alpha@@sub H2@. The values for E@super d@@sub OH@ (@theta@) were calculated as a function of @alpha@@sub H2@. Results of sensitivity analysis and rate of production calculations using this model imply that the main water-forming reaction on Pd at 1300 K is the hydrogen addition reaction H+OH ->H@sub 2@O.

SS-TuP51 What Can We Learn from Core Level Spectroscopy Studies of Ice?*, **D. Nordlund**,* Stockholm University, Sweden*; H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; M. Odelius, M. Cavalleri,* Stockholm University, Sweden*; P. Wernet,* BESSY, Sweden*; M. Nagasono,* Kyoto University, Japan*; B. Brena, M. Nyberg, L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

Core level spectroscopy is a powerful tool to obtain information on the unoccupied and occupied valence electron structure. The sensitivity of the valence electronic structure of water to different local H-bond situations is presented, where ice is used as a model system to approach important scientific aspects such as the local structure of liquid water, nature of the hydrogen bond, radiation induced ultrafast dissociation of water, and electron delocalisation and trapping processes. A number of experiments are presented together with spectral calculations based on density functional theory, revealing important information on the above listed aspects.

SS-TuP52 Self-Organized Growth of Nanopucks on 2D Pb Quantum Islands*, **Y.P. Chiu**,* National Taiwan Normal University, Taiwan*; H.Y. Lin, L.W. Huang,* Academia Sinica, Taiwan*; C.S. Chang,* Academia Sinica, Taiwan, Taiwan, ROC*; T.T. Tsong,* Academia Sinica, Taiwan

Self-organized growth is an attractive approach where a large number of structures can be formed simultaneously. The drawback for this approach involves the apparent difficulty in control of the structureâ?Ts size, their chemical homogeneity, and spatial arrangement. Several routes were taken to search for suitable templates on which the self-organized growth could be made tangibly practical. Regular strain-relief dislocations, periodic surface reconstructions, and Morie patterns have all been applied in attempt to improve the quality of self-organized growth. In this work, we employ the superstructures (electronic MoirÃ¨ patterns) found on 2D lead (Pb) quantum islands as a template to further grow self-organized 2D clusters (nano-pucks) of various materials. These patterns, originating from charge redistribution in the island in response to the lattice-mismatch-induced interfacial potential variation, thus differ from structure-driven templates. The boundaries of the periodic pattern are apparently repulsive for adatom diffusion. The activation energies for defining the template strength in trapping surface atoms have been obtained, which provide the practical parameters for controlling the size and spatial distribution of the nanopucks. A bi-layer complementary alternating behavior, similar to the confinement-induced phenomenon found in Pb quantum islands, also occurs in the growth of Ag nanopucks on the Pb islands of various thicknesses.

Surface Science
Room 210B - Session SS1-WeM
Metal Oxides and Clusters I: Formation and Structure

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS1-WeM1 The Chemistry of Au Clusters Supported on Titania: Early Steps Towards Understanding the Mechanism of Propene Epoxidation***, G. Mills, S. Chretian, V. Shapovalov,* ***H. Metiu,*** University of California, Santa Barbara **INVITED**

We use density functional calculations to try to increase our understanding of the interactions of hydrogen, oxygen, propene, and propene oxide with gold clusters in gas phase, with titania, and with gold clusters supported on titania. Our goal is to clarify the mechanism of propene epoxidation. I will also report briefly on a collaboration with Martin Moskovits concerning the modification of catalytic activity of CO oxidation, by manipulating the electron density in tin oxide nanowires.

9:00am **SS1-WeM3 Surface and Subsurface Oxidation of Ni(100) and Ni(111) Studied by Medium Energy Ion Scattering***,* ***M.A. Muñoz-Márquez,*** University of Warwick, UK, United Kingdom*; R.E. Tanner, D.P. Woodruff,* University of Warwick, UK

Using medium energy ion scattering (MEIS) and specifically 100 keV H@super +@ incident ions, the oxidation of the Ni(100) and Ni(111) surfaces have been investigated at temperatures around 200-300°C and with oxygen exposures up to 6000 L. This treatment range corresponds to that typically used to produce well-defined NiO(100) surfaces on Ni(100) and involves significantly thicker oxide formation than has been investigated by conventional surface science techniques in the past. The potential of MEIS to probe the deeper subsurface is highly relevant in these studies, as oxide formation >100 Å is seen on Ni(111). While it is well-established that the earliest stages of oxidation occur at lower exposures on Ni(111) than Ni(100), attributed to site blocking in the different chemisorbed oxygen phases on the two surfaces, our results show that this greater reactivity of Ni(111) persists to rather deep oxidation. Throughout these oxide films the stoichiometry of NiO is retained. Through the use of 'double-alignment' scattering geometries and qualitative LEED, the crystallography of these oxide layers has been investigated. LEED shows that on Ni(111) two (of the possible three) orientational domains of NiO(100) form, attributed to a slight misorientation of the surface. In general, the average crystalline registry with the bulk is poor, although at intermediate exposures a surprising result is that the outermost layers appear better-ordered than the near sub-surface. This is attributed to the probable influence of thick islands of limited lateral extent which causes the more penetrating ions to pass through differently oriented oxide islands. On Ni(111) simulations using the VEGAS code confirm that the data are consistent with this rationale. On Ni(100), the apparent poor order can also be reproduced in simulations assuming the NiO(100) crystallites are tilted on the surface as previously proposed on the basis of SPA-LEED investigations.

9:20am **SS1-WeM4 Thermodynamics of Pd(111) Oxidation from 10@super -7@ to 25 Pa: An In-Situ Photoemission Study***,* ***D.F. Ogletree****, G. Ketteler, H. Liu, E.L.D. Hebenstreit, H. Bluhm, M. Salmeron,* Lawrence Berkeley National Laboratory

The oxidation of Pd(111) has been studied in equilibrium with oxygen gas between 10@super -7@ and 25 Pa over a temperature range of 300 to 925 K. The experiments were carried out in a newly commissioned, second-generation high pressure photoemission spectroscopy (HPPES) system operating at the Molecular Environmental Sciences synchrotron beamline@footnote 1@. After UHV sample cleaning, the Pd(111) crystal was transferred to a variable pressure experimental cell coupled to a differentially pumped electron spectrometer. High resolution photoemission spectra were recorded for the Pd 3d@sub 5/2@, O1s/Pd3p@sub 1/2@ and valence band regions at different combinations of oxygen pressure and sample temperature. Dynamic and reversible changes in surface oxidation were observed in response to changes in the thermodynamic environment of the palladium substrate. An analysis of the thermodynamics and kinetics of the palladium-oxygen system will be presented. @FootnoteText@ @footnote 1@ Beamline 11.0.2 at the LBNL Advanced Light Source, Berkeley, CA USA.

9:40am **SS1-WeM5 Oxidation of Pt(111) by Gas-Phase Oxygen Atoms***,* ***J.F. Weaver****, A.L. Gerrard, J.J. Chen,* University of Florida

The oxidation of Pt(111) by an atomic oxygen beam has been investigated as a function of surface temperature using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (ELS). For oxygen coverages below about 0.50 ML (where 1 ML = 1.5 x 10@super 15@cm@super -2@), the rate of atomic oxygen adsorption is found to be insensitive to surface temperature over the range from 150 to 450 K. After 0.5 ML of atomic oxygen is adsorbed, the oxidation rate decreases with decreasing temperature, and the oxygen coverage saturates at values that also decrease with decreasing temperature. At the highest temperature investigated (450 K), the oxygen coverage at saturation is about 2 ML, whereas only 0.25 ML can be generated by dissociatively adsorbing O@sub 2@ on Pt(111) in ultrahigh vacuum. The mechanism for Pt(111) oxidation involves the initial formation of a chemisorbed layer, within which the oxygen atoms experience significant repulsive interactions after the coverage is increased above 0.25 ML. Long-range order in the high-coverage adsorbed layer could not be observed with LEED. At each surface temperature investigated, islands of platinum oxide begin to form after the oxygen coverage exceeds about 0.5 ML. TPD and ELS data suggest that the oxide islands grow three-dimensionally at surface temperatures ranging from 150 to 450 K, and that their formation is accompanied by the regeneration of metallic regions on which additional oxygen adsorbs and subsequently incorporates into growing islands. The kinetics of the oxidation process and the reactivity of the surface oxygen phases will also be discussed.

10:00am **SS1-WeM6 Thermodynamically Controlled Self-Assembly of Oxide Nanostructures@footnote *@***,* ***F.P. Netzer****, J. Schoiswohl, M Sock,* University of Graz, Austria*; G. Kresse,* University of Vienna, Austria*; S. Surnev, M.G. Ramsey,* University of Graz, Austria

The fabrication of surface-supported nanoscale oxide materials in low dimensions via a chemically driven self-assembly process of novel oxide cluster molecules is reported. As opposed to usual molecular self-assembly, where the construction units are deposited directly from the gas phase, the oxide building blocks with a unique stoichiometry and structure form spontaneously on a Rh(111) metal surface. These can be organised into different two-dimensional oxide structures by careful adjustment of the chemical potential of oxygen µ@subO@, allowing the controlled design of oxide nanostructures on a metal surface. This is demonstrated by following, at the atomic level, the formation and aggregation of planar vanadium oxide V@sub6@O@sub12@ clusters. The planar V@sub6@O@sub12@ cluster molecules form under appropriate conditions of µ@subO@ and of the vanadium concentration at the Rh(111) surface. The structure and stability of these hexagonal V@sub6@O@sub12@ clusters have been elucidated by STM and density functional theory (DFT) calculations. The V@sub6@O@sub12@ structures do not exist in the gas phase and constitute a novel kind of cluster material, that is stabilised by the metal-cluster interface. The V-oxide clusters are mobile at elevated temperature and their surface diffusion has been studied in variable-temperature STM experiments: the diffusion parameters indicate diffusion of the entire clusters. The V@sub6@O@sub12@ units can be organised by self-assembly into different 2D oxide structures, depending on µ@subO@. The assembly process occurs via a reductive or oxidative condensation process, which involves strong chemical bonding interactions with partly covalent and ionic character. Nevertheless, the here reported aggregation is reversible, and by adjustment of µ@subO@ and the Rh surface temperature the V@sub6@O@sub12@ clusters can be regenerated from the oxide islands by 2D re-evaporation. @FootnoteText@ @footnote *@ Work supported by the Austrian Science Funds.

10:20am **SS1-WeM7 STM/AFM Study of WO@sub 3@ Cluster Growth on Highly-Oriented Pyrolitic Graphite***,* ***O. Bondarchuk,*** University of Texas at Austin*; Z. Dohnalek, B.D. Kay, J. Kim,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin

With the ultimate goal of understanding the catalytically activity of WO@sub 3@ clusters supported on oxide surfaces, we have investigated WO@sub 3@ deposition on highly-oriented pyrolitic graphite (HOPG) using in-situ scanning probes. Our efforts were aimed at understanding how the WO@sub 3@ cluster size and morphology depend on deposited amount and substrate temperature. In this work we have studied tungsten oxide films grown on HOPG substrate at temperatures ranging from 300 to 650 K and having thickness from submonolayer up to ~1 µm. STM images of WO@sub 3@clusters formed from submonolayer WO@sub 3@ deposition at room temperature show fractal-like shape. This shape suggests that a diffusion-limited aggregation mechanism governs the growth. Scanning tunneling spectroscopy indicates that the WO@sub 3@ clusters are semiconducting in nature. Tip induced effect leading to complete removal of WO@sub 3@ clusters from HOPG are observed upon extended scanning. In contrast, non-contact AFM imaging does not does not perturb the WO@sub 3@clusters. Possible mechanisms of the tip induced removal of WO@sub 3@ on HOPG will be discussed. Deposition of a submonolayer amount of WO@sub 3@ at ~ 600 K leads to the formation of WO@sub 3@ needle like crystallites of relatively uniform width (~15-20 nm) and length (~100-300 nm). The crystallites are mostly attached to the steps indicating that steps are the preferred nucleation centers. The needle-like growth of WO@sub 3@ crystallites persists even for thicker deposits (~ 1 µm). Ex-situ X-ray diffraction (XRD) analysis performed on thick films suggests that the WO@sub 3@ crystals have cubic symmetry. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

10:40am **SS1-WeM8 Surface and Interface Analysis of MgxZn1-xO for Cubic, Hexagonal and Intermediate Phases by X-Ray Photoelectron and Rutherford Back Scattering Spectroscopies**, *S. Hullavarad,* University of Maryland*; R. Vispute,* Bluewave Semiconductors, Inc.*; S. Dhar, T. Venkatesan, **I. Takeuchi**,* University of Maryland

MgZnO has attracted increased attention for its unique properties of existence in multiphases either in hexagonal for 0<Mg<0.35 or cubic for 0.35<Mg<1 in MgxZn1-xO. This material is of significant importance for various applications in flame sensors, UV index monitors and missile plume detection. The presence of Mg with a composition of 0-100% in ZnO lead to higher bandgaps ranging from 3.6eV to 7.8 eV of resulting MgZnO. This allows picking up desired Mg composition corresponding to suitable UV sensitive window and growing on lattice matched substrate. In this study we have picked up three Mg compositions representing hexagonal, cubic and intermediate regions. The samples are characterized by X-Ray Diffraction, Rutherford Back Scattering techniques for crystalline quality, and composition of the films. UV-Visible spectroscopy is used for analyzing the optical property of MgZnO films. In this work we emphasize the role of surface and interface in quality of material from crystal structure, grain boundary related defects and the cumulative effect on devices fabricated on such materials by surface sensitive study carried out using X-Ray Photoelectron and interface study by Rutherford Back Scattering spectroscopy.

11:00am **SS1-WeM9 Novel Stages of Growth of Metal Oxide Nanodots: Cu2O on SrTiO3(100)@footnote 1@**, ***I. Lyubinetsky**, A.A. El-Azab, A.S. Lea, S.T. Thevuthasan, D.R. Baer,* Pacific Northwest National Laboratory

Although similar to semiconductor nanostructures in some ways, oxide nanodots have been observed in greater structural variations. Here we report on a significant difference in the growth process which exhibits novel stages. Self-assembled formation of the crystalline cuprous oxide (Cu2O) nanodots on the SrTiO3(100) substrate has been carried out using oxygen plasma assisted MBE and evaluated by XPS, AES, XRD and AFM. Selective formation of the nanodots of single Cu2O-phase occurs only in a very narrow growth parameter window, in comparison with the bulk phase diagram. Formation of Cu2O nanoclusters (with the size range of 10-50 nm) may be described as progressing through several stages. Unlike lattice-mismatched heteroepitaxy in the majority of semiconductor systems, initial stages of the growth of oxide nanodots proceed without formation of the wetting layer. Already at sub-monolayer coverages, small, truncated square Cu2O dots start to form. At next, novel stage a continued deposition leads to increase of the dot density, not the size, and results in reaching a critical dot density, upon which larger nanoclusters start to grow. Resulting morphology consists of large islands on top of the closed-packed layer of the small nanodots. Using a kinetic model of film morphology development, we show that the larger island formation can be caused by small dot coalescence, driven by fluctuation of island-island separation at increased dot density. Under different surface conditions of the SrTiO3(100) substrate (high temperature annealed, perfect TiO2-terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nanodot distribution have been observed. @FootnoteText@ @footnote 1@ This work was jointly supported by the Department of Energy (DOE), Basic Energy Sciences Division and the Laboratory Directed Research and Development at PNNL, which is operated by Battelle for the DOE.

11:20am **SS1-WeM10 Surface Stability of Epitaxial SrRuO@sub 3@ Films**, ***A.P. Baddorf**,* Oak Ridge National Laboratory*; J. Shin,* The University of Tennessee*; S.V. Kalinin,* Oak Ridge National Laboratory*; R.G. Moore,* The University of Tennessee*; H.N. Lee, H.M. Christen,* Oak Ridge National Laboratory*; E.W. Plummer,* The University of Tennessee

Strontium ruthenium oxide, SrRuO@sub 3@, may play an important role in oxide electronic devices because of its metallic nature and lattice constant compatible with many transition metal oxide perovskites. Use in device fabrication requires excellent surface and interface stability without reduction or loss of volatile oxides. Thin films of SrRuO@sub 3@ appear to be quite stable, retaining their crystalline nature, as observed with electron diffraction, even after exposure to atmosphere. Surprisingly, this stability disappears after annealing in vacuum to only 200@degree@C. We have studied the surface stability of epitaxial SrRuO@sub 3@ films using a combination of electron spectroscopies, diffraction, and scanning probe microscopy. Epitaxial SrRuO@sub 3@ thin films were grown by pulsed laser deposition using a stoichiometric target on (001) SrTiO@sub 3@ substrates. Atomic force microscopy images taken in air confirm the high quality of the films, showing uniformly spaced terraces with single steps on the film surface, which closely imitate those of the SrTiO@sub 3@ substrate. After reinsertion into vacuum, a (1x1) Low Energy Electron Diffraction (LEED) pattern has been observed at room temperature, revealing an excellent chemical stability in air. The LEED pattern disappears after a brief anneal in vacuum at 200@degree@C, indicating surface disordering. Films were annealed in high vacuum in steps of 100@degree@C up to 800@degree@C and studied after cooling by LEED, x-ray photoelectron spectroscopy, scanning tunneling microscopy and thermal desorption spectroscopy. Loss of SrO from the surface leads to surface pitting and then balling of metallic Ru at temperatures below 400@degree@C. Vibrational spectroscopy relates this monolayer decomposition to submonolayer concentrations of surface hydrocarbons. Stabilities are compared with in-situ films in a new chamber combining high pressure growth with surface characterization.

11:40am **SS1-WeM11 Effect of Polarization on Reactivity of BaTiO@sub 3@ (100)}**, ***J. Garra**, B. Halevi, J. Vohs, D.A. Bonnell,* The University of Pennsylvania

Surface reactivity of ferroelectric compounds is an important component of a new approach to nano lithography, may be an interesting catalytic support, and is indicated in ferroelectric memory failure. In order to examine the relationship between atomic polarization and surface adsorption, reactions with single crystal BaTiO@sub 3@ (100) were characterized by temperature programmed desorption, x-ray photo emission spectroscopy, scanning surface potentiometry, and piezo response force microscopy. Similar to the case of other perovskite oxides, water does not adsorb at room temperature or above unless the surface contains a high density of defects. Adsorption of CO2 on BaTiO3 is more complex than on SrTiO@sub 3@. The domain orientation dependence of these reactions will be discussed in the context of proposed reaction mechanisms.

Surface Science

Room 210C - Session SS2-WeM

Semiconductor Surface and Interface Structure

Moderator: A.A. Baski, Virginia Commonwealth University

8:20am **SS2-WeM1 Atomic Structure Determination of @beta@-SiC(001)-(3x2): Experiment and Calculations**, *A. Tejeda,* Universidad Autonoma de Madrid, Spain*; D. Dunham,* Northern Illinois Univ.*; F.J. Garcia de Abajo,* CSIC-UPV/EHU and DIPC, Spain*; J.D. Denlinger, E. Rotenberg,* Ernest Orlando Lawrence Berkeley National Lab*; **E.G. Michel**,* Univ. Autonoma de Madrid, Spain*; P. Soukiassian,* Commissariat a l'Energie Atomique and Northern Illinois Univ.

Silicon carbide is a IV-IV compound wide band-gap semiconductor with multiple technological applications. The structure of the Si-rich 3C-SiC(001)-(3x2) surface reconstruction is determined using soft x-ray photoelectron diffraction. Photoelectrons are detected along a full hemispherical sector for different photon energies. The experimental intensity modulations were compared in this work with the results of a suitable scattering formalism that simulates the measured PED by modeling the structure of the last atomic layers. A spherical-wave multiple-scattering cluster formalism was used to reproduce the data and discern the correct surface structure of Si-rich 3C-SiC(001)-(3x2), obtained from a systematic search between the models proposed in the literature. The favored model is a modified version of the two-adlayer asymmetric dimer model (TAADM). An R-factor analysis has been employed to refine this model. We determine the interlayer spacings of the last six atomic layers and find a corrugation of 0.25 Å for the atoms in the outermost dimer. Atoms in the layer underneath dimerize as well, with alternating long and short bond lengths. The long-and-short alternateness between dimer bond lengths explains the top dimmer asymmetry along one single direction. The dimerization takes place through lateral relaxation, without large vertical distortions. The third atomic layer is also dimerized, with a dimer bond length of 2.43 Å. We conclude our results, together with STM and GIXRD experiments, converge in a unifying model for the 3C-SiC(001)-(3x2) surface.

8:40am **SS2-WeM2 Identification of Si and Ge on the Hydrogen-Terminated Ge/Si(001) Surfaces for Observation of Intermixing**, ***Y. Fujikawa****, A. Kuwano, M. Kawashima, Y. Yamada-Takamura, T. Nagao, T. Sakurai,* Tohoku University, Japan

Control of the local composition of SiGe films in an atomic level is of great technological importance for designing the SiGe nanodevices. Intermixing effect between Si and Ge is the key issue to achieve precise composition control at the surface layer. It has been known that hydrogen-rich condition at ~300 degree C induces segregation of Si to the surface layer on the Ge covered Si(001) surface, while Ge prefers to stay at the surface layer without hydrogen@footnote 1@. This result implies that the hydrogen-annealing treatment is a useful method to control the composition of SiGe surface layer. We investigated the hydrogen-terminated Ge/Si(001) surface using STM to find that Ge-H sites are imaged as brighter protrusions in comparison with Si-H sites under the empty-state imaging condition. This effect is similar to the case of Cl-terminated Ge/Si(001) surface, which was observed recently@footnote 2@. Si-H and Ge-H sites on the hydrogen-terminated Ge/Si(001) with a Ge coverage of 1.5 ML were resolved successfully using this empty-state imaging condition to study the atomic process of intermixing. Furthermore, it turned out that the Si segregation by the hydrogen-annealing produces significantly bright features beside the dimer-row vacancies (DVLs), in addition to the features coming from Ge-H and Si-H sites. This feature can be attributed to the broken rebonded structure inside the DVL, which contributes the re-adjustment of the surface strain which is modified by the Si segregation. @FootnoteText@ @footnote 1@ Rudkevich et al., Phys. Rev. Lett. 81, 3467 (1998).@footnote 2@ Lin et al., Phys. Rev. Lett. 90, 046102 (2003).

9:00am **SS2-WeM3 The Surface of Silicon-on-Insulator: Structure, Stress, and Three-Dimensional Nanocrystals**, ***M. Lagally***, University of Wisconsin-Madison **INVITED**

Future generations of silicon devices will require approaches beyond the conventional in terms of both fabrication and characterization. In particular, instead of bulk Si, most devices will use silicon-on-insulator (SOI) or variants, such as strained-Si-on-insulator (sSOI), SiGe-on-insulator (SGOI), Si-on sapphire (SOS), and so forth, where in all cases a very thin crystalline layer of Si or SiGe is bound to an oxide or other insulator. Whereas the potential technological value of these materials is without question, what roles do the vacuum-Si and oxide-Si interfaces play? Is there anything interesting that has not already been discovered in the many years in which Si surfaces have been studied? We describe some interesting behaviors. Most important is the presence of strain and the essential instability of the very thin crystalline layer (called the template layer) resting on an oxide. Under appropriate conditions the template layer can dewet, agglomerate, and self-organize into an array of Si nanocrystals. Using LEEM, we observe this process and, with the help of first-principles total-energy calculations, we provide a quantitative understanding of this pattern formation and show how addition of Ge affects the energies and hence the pattern. We have been able to image the surface of SOI with STM, providing insights into the surface structure. Growth of heteroepitaxial films on SOI brings with it unique defect generation mechanisms that are associated with the Si-oxide interface, and a bending of the template that is counterintuitive. We fabricate thin membranes and free-standing structures to investigate the effect of added uniaxial stress on adatom diffusion and the nucleation and coarsening of 2D and 3D structures on this surface. Aspects of the work are supported by NSF, DARPA, ONR, and DOE.

9:40am **SS2-WeM5 Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development**, ***G.J. Xu***[1], *J.H. Weaver,* University of Illinois at Urbana-Champaign

Scanning tunneling microscopy results show the consequences of Si adatom deposition onto Br-saturated Si(100)-(2x1). Those adatoms undergo an exchange reaction with Br but they are immobile at room temperature. In the low coverage regime, annealing to 650 K leads to dimerization, limited ordering, and the formation of short Si chains. Adatom capture by those chains produces features of even and odd numbers of atoms. Annealing at 700 K eliminates the odd chains, but diffusion is highly constrained by Br site blocking. With increased Si coverage, there is further nucleation of chains and chain growth. The local patterning of the Si chains reveals the influence of the strong steric repulsive interactions of Br as out-of-phase structures were favored over in-phase structures around any given chain. Eventually, those interactions favor adlayer (3x2) patches rather than (2x1) islands. Second layer chains appear after the deposition of ~0.3 ML, with layer-2 nucleation at antiphase domain boundaries of layer-1. Bromine loss was observed, even at 650 K, and it is probably tied to the dynamics of atom exchange involved with Si diffusion on a saturated surface.

10:00am **SS2-WeM6 Vacancy Induced Nano-Wire Structure of Ga@sub 2@Se@sub 3@ on Si(100)**, ***T. Ohta****, D.A. Schmidt, C.Y. Lu, Q. Yu, M.A. Olmstead, F.S. Ohuchi,* University of Washington

We report formation of nano-wire structure of gallium-selenide (Ga@sub 2@Se@sub 3@) grown on arsenic terminated silicon (Si) (100). Ga@sub 2@Se@sub 3@ crystallizes into a defected zinc-blende structure with every third of the Ga site vacant. Vacancies are necessary to maintain charge neutrality in the crystal, and are responsible for its highly anisotropic electrical and optical properties by ordering into line geometry. Scanning tunneling microscopy (STM) revealed that wire structure is two-unit-cell-wide with the separation between wires of about three-unit cell, and its direction is influenced by alternating symmetry of the initial substrate. We will discuss its atomic structure, evolution of its initial growth and the interface structure between Ga@sub 2@Se@sub 3@ and Si, based on our recent investigation using STM and core-level photoemission spectroscopy (PES). It is shown that the formation of the wire structure is strongly related to the ordering of structural vacancies, and we will present its growth model. This formation mechanism is unique to the prevalence of structural vacancies incorporated in Ga@sub 2@Se@sub 3@, unlike other nano-structure formation mechanisms driven by defects or strain, such as for InAs nanodots on GaAs or SiGe clusters on Si. This work is supported by NSF Grant DMR 0102427 and M. J. Murdock Charitable Trust. T. O. further acknowledges support from University Initiative Fund of the University of Washington, and D. A. S., UW-PNNL Joint Institute for Nanoscience research award.

10:20am **SS2-WeM7 STM Study of Silicon Surfaces at P-N Junctions Prepared by Low-Temperature Processing**, ***T.-C. Shen,*** Utah State University*; J.S. Kline, J.R. Tucker,* University of Illinois at Urbana-Champaign

Dopant distribution at p-n junctions has been extensively studied by many techniques. Recent advance of electron devices further demands a thorough understanding and precise control of the dopant behavior at nanometer scale. Feenstra et al. pioneered the technique of cross-sectional STM to image the p- and n-type GaAs interface. To examine planar p-n junctions in Si, conventional high temperature surface preparation in ultrahigh vacuum is not suitable due to enhanced dopant diffusion and desorption. In this presentation, we report some of our experimental findings based on a previously developed low-temperature surface preparation technique involving 300eV Ar ion sputtering and 600-700°C annealing. The B-doped substrates used in this work are either at an impurity level of 3x10@super 17@ cm@super -3@ or 1x10@super 19@cm@super -3@. N-type patterns are fabricated by implanting 40-50 keV As ions at a dose of 1x10@super 15@cm@super -2@ into the B-doped substrates. The atomically clean and flat surfaces prepared at low temperatures allow us to obtain atom-resolving images both in the As-implanted region and the B-doped substrate as well as their original interface. We observe for the first time that heavily B-doped substrates lead to c(4x4) patterns on the surface the same as the result of diborane exposure. When terminating the surface with H, we find that the dangling bonds in the As-region are much brighter than those on the substrate. More c(4x4) regions and less C and H-induced clustering are observed in the As region. Surface topography at different annealing conditions, the role of dopant atoms in the diffusion of other impurities and their

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

electronic effect will be discussed. This work is supported by DARPA-QuIST program under ARO contract DAAD 19-01-1-0324.

10:40am **SS2-WeM8 Hydrogen Interaction with a Si(113)-3x2 Surface*, M. Yoshimura*,** *K. Mamiya, K. Ueda,* Toyota Technological Institute, Japan

Since the Si(113) surface is thermally stable and has a low energy compared to that of the low-index surfaces such as Si(111) and Si(001), it is expected to a good substrate for epitaxy in semiconductor technology. The clean surface reconstructs into a 3 x 2 superstructure consisting of pentamers and adatoms, as was proposed by Dabrowski et al.@footnote 1@ Each 3 x 2 cells contain a subsurface interstitial located below one of the tetramers, which lowers the total surface energy. On the other hand, hydrogen termination is one of important techniques in the silicon-based device processes. However, hydrogen interaction with the Si(113) has been studied only by spectroscopic measurements such as electron energy loss spectroscopy (EELS)@footnote 2@. Here, we report ultrahigh vacuum scanning tunneling microscopy (UHV-STM) study of the atomic hydrogen adsorption onto the clean Si(113)-3 x 2 surface on an atomic scale. A Si(113) surface was cleaned by a conventional procedure and was exposed at room temperature to atomic hydrogen by cracking of hydrogen molecules using a hot tungsten filament. After 10 L exposure, the reduction in the density of states around Fermi level was confirmed by scanning tunneling spectroscopy (STS). STM images revealed clearly that some adatoms were missing and some pentamers changed their image contrast, probably due to hydrogen adsorption at the surface dangling bonds of the corresponding sites. The clustering was not observed up to this exposure level. Based on the results of STM/STS together with low-energy electron diffraction (LEED), we discuss the initial adsorption processes of atomic hydrogen on Si(113)-3x2 at an atomistic level. @FootnoteText@ @footnote 1@ J. Dabrowski et al., Phys. Rev. Lett. 73 (1994) 1660.@footnote 2@ K. Jacobi and U. Meyer, Surf. Sci. 284 (1993) 223.

11:00am **SS2-WeM9 Application of the Simplified Bond-Hyperpolarizability Model to Bulk Second- and Third-Harmonic Generation in Semiconductors*, H.J. Peng*,** *E.J. Adles, D.E. Aspnes,* North Carolina State University

Application of nonlinear optical (NLO) spectroscopies to the analysis of surfaces and buried interfaces of crystalline semiconductors requires an understanding of the contributions from the second- and third-harmonic generation (SHG, THG) from the bulk. THG is particularly relevant because for reasons of macroscopic symmetry THG is the lowest NLO effect that can be used to study the surfaces and interfaces of (001)Si, which underlies integrated-circuits technology. We show that the simplified bond-hyperpolarizability (SBHM) model that we previously developed to analyze surface and interface contributions to second- and fourth-harmonic generation data for Si provides an accurate description of bulk THG of Si with no adjustable parameters beyond amplitude scaling. The SHG contribution, which is nominally forbidden in Si, can be evaluated from the known linear-optic response and, contrary to some speculation, is found to be negligible for this material. These results are expected to be applicable to other semiconductors as well, thereby simplifying the analysis of surfaces and interfaces by NLO techniques.

11:20am **SS2-WeM10 Second Harmonic Generation from Metallic Quantum Wells on Si(111) Surfaces*, K. Pedersen*,** *T.G. Pedersen,* Aalborg University, Denmark*; P. Morgen,* SDU Odense University, Denmark

Optical second harmonic generation (SHG) from materials with bulk centrosymmetry such as metals and a number of elemental semiconductors is surface and interface sensitive due to the lack of electric dipole contributions to second-order nonlinearities in the bulk of such materials. Thin films on a substrate, having two dissimilar boundaries, are thus expected to be interesting objects for SHG studies. The buried interface can be reached even through 50 to 100 layers of metal but the interface signal appears coherently added to contributions from the free surface. Resonant electronic transitions that may appear in SHG spectroscopy can thus be localized either at the free surface or at the buried interface. Under proper growth conditions thin metallic films on semiconductors form crystalline layers showing sharp quantum well (QW) levels in photoemission spectroscopy. In SHG the discrete QW levels result in oscillating signals as the system passes through a series of resonant transitions between occupied and empty states for growing film thickness. In the present work electronic transitions at the buried interface are identified through the dispersion of quantum well resonances seen with SHG. Recordings of SHG from a wedge shaped Ag film (0-50 layers) grown on Si(111)7x7 surface show that resonances disperse toward lover thickness for growing photon energy. Shifts or breaks in dispersion curves appear when the phase of the interface signal changes at resonant electronic transitions. In addition to expected transitions near critical points of bulk Si an interface resonance is found between the two lowest critical points of bulk Si.

11:40am **SS2-WeM11 Spectroscopic Second Harmonic Generation on Hydrogenated Amorphous Silicon Surfaces and Interfaces*, C.M. Leewis*,** *J.J.H. Gielis, I.M.P. Aarts, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Optical Second Harmonic Generation (SHG) is applied on hydrogenated amorphous silicon (a-Si:H) films on fused silica substrates to investigate the presence of surface and buried interface dangling bonds. For amorphous material, e.g. a-Si:H, the SHG technique is surface-specific and therefore originates from both the film surface and the film-substrate interface. The origin of the second harmonic signal can be due to dangling bonds and strained bonds. In addition, optical interference effects can enhance the signal for certain wavelength-film thickness combinations. The technique is applied both ex situ, and in situ in a UHV setup on hot wire grown films. An incident polarization scan is performed for both p- and s-polarized SHG radiation while SHG is also measured while rotating the sample around the axis normal to the substrate. It has been established that the SHG can be described by the infinity-m symmetry class, which is in agreement with the amorphous nature of the material. In situ spectroscopic scans are performed with a probe photon energy in the range 1.0-1.6 eV for different polarizations. These scans are in agreement with ex situ scans on plasma deposited a-Si:H. The observed resonant peaks correspond possibly to surface and interface dangling bond states@footnote 1@. The presence of dangling bonds is investigated with real time measurements. These experiments during film growth have already shown that the SHG intensity increases instantly when growth is started, and gradually decreases during further growth. In addition, it is shown that the maximum SHG intensity increases for increasing substrate deposition temperatures in the range 520-720 K. The consequences for a possible surface and interface concentration of dangling bonds will be discussed. @FootnoteText@ @footnote 1@Pedersen et al., Phys. Rev. B 52, R2277 (1995).

Surface Science
Room 213B - Session SS+OF-WeA
Contacts to Molecules and Molecular Films

Moderator: G.G. Malliaras, Cornell University

2:00pm **SS+OF-WeA1 Electron Transport at Interfaces and Junctions: Understanding Molecular Electronics***, **X.-Y. Zhu,*** University of Minnesota **INVITED**

Charge transport at or across molecule-electrode interfaces is central to the operation of a wide variety of molecule-based electroic devices. The critical charge transporting interfaces in most systems are buried interfaces which are not readily accessible to conventional structural or spectroscopic probes. For any given device, two critical questions are: (1) What is the structural and chemical nature of the molecules at the buried interface before or during operation? (2) How is the electrical conductance across an interface related to physical properties such as electronic energy level alignment and charge redistribution? This talk will attempt to address both questions from spectroscopic measurements and to demonstrate that such a spectroscopic view is of critical importance in achieving a quantitative understanding of moleular electronics.

2:40pm **SS+OF-WeA3 The Influence of Chemical Coupling Groups on the Electronic Structure of Conjugated Self-Assembled Molecular Monolayers***, **S.W. Robey**,* NIST*; C.D. Zangmeister,* NIST, US*; R.D. Van Zee,* NIST

The performance of conjugated molecular systems in electronic applications, either for organic light emitting diodes (OLED's) and field effect transistors, or in more speculative applications proposed for molecular electronics, depends critically on coupling at the molecule-electrode interface. Interactions at this interface determine the alignment of the contact Fermi level with the transport levels in the molecular system, which in turn controls charge injection into the molecular @pi@ levels. Using one-and two-photon photoemission to access occupied and unoccupied levels, we have examined the influence of the metal-molecule coupling chemistry on the Fermi level alignment and electronic structure in the prototypical "molecular wire", 4,4'-(ethynylphenyl)-1-benzenethiol system on Au. Photoelectron spectroscopies reveal an increase in the binding energies (relative to the Fermi level of Au) for the C @sigma@ and @pi@ derived valence levels and the C (1s) core level upon substitution of the isocyanide coupling for thiol. No spectral changes are observed, however, in the region of the molecular @pi@ levels important for transport. Optical absorption measurements also reveal no change in optical band gap. These results indicate that substitution of the isocyanide linking chemistry for thiol based chemistry leads to a large shift, by ~ .5 eV, of E@sub f@ away from the highest occupied level in the molecule, but little modification of the extended @pi@ molecular electronic structure. The interaction at the Au-thiol-OPE interface will be compared and contrasted with the Au-isocyanide-OPE interface in terms of bonding and charge transfer effects and contact made to RAIRS and transport data for related systems.

3:00pm **SS+OF-WeA4 Mechanical and Charge Transport Properties of Self Assembled Organic Monolayers***, **I. Ratera**, J.Y. Park, J. Chen, A. Liddle, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We are interested in measuring and correlating electronic and mechanical properties of molecules. We will report our progress in the fabrication of insulating test substrates with embedded coplanar metallic nanoelectrodes. In this manner a monolayer of molecules can bridge two electrodes and be accessible to an AFM or STM tip. This approach may lead to a better understanding the nature of the molecule - electrode contact. The use of AFM with conducting tips provides the ability to vary the load on the nano-contact and also opens the way for exploring electron transfer as a function of molecular deformation. Initial results will be presented on the influence of mechanical stress on the structural and electrical properties of self-assembled alkylthiols on gold surfaces as a function of the chain length and tip pressure.

3:20pm **SS+OF-WeA5 Electronic Properties of Interfaces between Organic Semiconductors and Metals***, **M. Knupfer,*** Leibniz Institute for Solid State and Materials Research Dresden, Germany **INVITED**

The electronic properties and the energy level alignment of interfaces between organic semiconductors and metals have been studied using photoemission spectroscopy in the valence as well the core level region. Different contrubutions to the frequently observed interface dipoles are discussed. In particular, the role of a reduction of the metal workfunction in comparison to clean, uncovered surfaces and image charge screening will be addressed. Furthermore, there are several examples where a charge transfer is observed at the interface, in particular for technologically relevant cases, which is essential for the understanding of charge transport acroos the corresponding interface.

4:00pm **SS+OF-WeA7 Energy Level Alignment at Organic Interfaces: Interface Induced Gap States and Charge Neutrality Levels***, **T.U. Kampen**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The energy level alignment at organic interfaces determines the efficiency of charge injection into organic films. Quite often the vacuum level alignment rule has been used to determine the energy level alignment at organic interfaces. Here, barrier heights can simply be calculated using the ionisation potentials or electron affinities of semiconductors materials and work functions of metals. For organic interfaces a conclusion has been reached that in general the vacuum levels do not align. At intimate, abrupt, and defect free interfaces of inorganic semiconductors interface induced gap states are the primary mechanism determining the energy level alignment. These interface states derive from the bulk states and their character changes across the band gap from more acceptor-like closer to the conduction band to predominantly donor-like nearer to the valence band. The branch point where the character changes has the significance of a charge neutrality level. This work shows that the concept of interface induced gap states may also be applied to organic interfaces. The charge neutrality levels of PTCDA, DiMe-PTCDI, and CuPc are found to be 1.96 eV, 1.93 eV, and 0.51 eV above the HOMO, respectively.

4:20pm **SS+OF-WeA8 Work Function and Charge Distribution XPS Study of Molecular Layers Self-Assembled on Gold***, H. Cohen, **S. Ray**, R. Naaman,* The Weizmann Institute of Science, Israel

Substrate-overlayer charge transfer frequently imposes considerable changes on the properties of self-assembled (SA) monolayers. The study of space charge distribution across molecular layers is targeted here, using XPS in a slightly modified setup, capable of in-situ work-function evaluation. Fine differentiation between chemical and electrical information across dipolar layers is demonstrated. Intra-molecular charge transfer is found to take place in part of the systems, giving rise to a directional flip of the dipole moment on the nanometer scale.

4:40pm **SS+OF-WeA9 Influence of Electrode Contamination on @alpha@-NPD/Au Hole-injection Barriers***, **A.S. Wan**, J.H. Hwang, A. Kahn,* Princeton University

Processing for OLEDs and other organic devices often involves exposure of surfaces and interfaces to nominally controlled atmosphere (e.g. N@sub 2@) or even ambient conditions. A model system for studying barriers built under such "practical" conditions, as opposed to barriers built on ultra-clean substrates prepared under ultra-high vacuum (UHV) conditions, is the interface between Au and @alpha@-NPD, a standard hole- transport material for OLEDs. In this work, we investigate the effect of ambient exposure of polycrystalline Au surfaces on the hole-injection barrier using ultraviolet photoemission spectroscopy (UPS) and I-V measurements. We compare @alpha@-NPD layers grown in UHV on: i. Au as-loaded, exposed to air; ii. Au cleaned by Ar@super +@ sputtering; iii. fresh Au deposited in UHV. Conventional wisdom is that the higher the work function of the contact metal, the lower the hole-injection barrier. However, our UPS studies unambiguously show that the injection barrier is 0.5-0.6 eV lower for Au exposed to air, which has a work function of 4.7-4.9 eV, than for clean Au (sputtered or UHV deposited), which has a work function of 5.3-5.4 eV. The vacuum level shift, or dipole barrier, (down from Au to organic) is 0.3 eV for the former and 1.3 eV for the latter. I-V measurements on Au/@alpha@-NPD/Au devices made on clean vs. "dirty" Au show several orders of magnitude increase in injection from "dirty" Au, entirely consistent with the changes in barriers measured in UPS. The large differences in dipole and injection barriers are attributed to the layer of contamination (consisting primarily of carbon) on the air- exposed Au, which lowers the work function of the metal and decouples the interface molecules from the Au atoms. Mechanisms based on disruption of interface bonding and/or metal-induced states will be discussed.

5:00pm **SS+OF-WeA10 Time-Evolution and Stability of Metal-Molecule Contacts***, G. Nagy, **A.V. Walker**,* Washington University in St. Louis

Understanding the nature of metal-molecule interactions is important for many technologies, including organic and molecular electronics. It has already been demonstrated using vapor-deposited metals on self-assembled monolayers (SAMs) that many interactions are possible, ranging from destruction of the SAM to organometallic formation to penetration through the SAM to the Au/S interface. We apply time-of-flight secondary ion mass spectrometry (TOF SIMS) experiments and density functional theory (DFT) calculations to investigate the time-evolution and the energetics of vapor-deposited metallic contacts. As model systems we are employing vapor-deposition of copper on alkanethiolate SAMs with -CH3, -OCH@sub 3@, -COOH, -OH and -COOCH@sub 3@ terminal groups. We observe at room temperature that vapor-deposited Cu on -COOH and -OCH@sub 3@ SAMs initially both penetrates to the Au/S interface and forms a weak complex with the terminal group. However, Cu at the vacuum interface is not stable in the long term and slowly penetrates through the monolayer. We demonstrate that the stability of metal-molecule contacts is dependent on a number of factors including the strengths of the metal-metal and the metal-molecule interactions and the rate of penetration through the monolayer, which itself is dependent on the diffusion of the SAM molecules on the Au substrate.

Surface Science
Room 210B - Session SS1-WeA
Metal Oxides and Clusters II: TiO@sub 2@ and Photocatalysis

Moderator: U. Diebold, Tulane University

2:00pm **SS1-WeA1 First-Principles Study of Intrinsic Defect Formation Energies in Tio@sub 2@***, J. He*, *S.B. Sinnott,* University of Florida

First-principles calculations are used to study intrinsic defects in bulk rutile TiO@sub 2@ and on the TiO@sub 2@ (110) surface. The approach is density functional theory (DFT) using the generalized gradient approximation (GGA) combined with plane-wave ultrasoft pseudopotentials. In particular, the formation energies of isolated vacancies, interstitials, and substituents with different charges, representing localized or distributed charge states, are evaluated. The DFT calculation results are combined with thermodynamic data to calculate the defect formation energies. In particular, the influence of temperature and oxygen partial pressure on the oxygen chemical potential is taken into account. The calculations suggest that fully charged Ti interstitials are more stable than oxygen vacancies at most oxygen partial pressures. Contrary to expectations, our preliminary results also indicate that the formation energy behavior of O vacancies at the TiO@sub 2@(110) surface is similar to the formation energy behavior of O vacancies in bulk TiO@sub 2@. These results are helping us to understand defect formation and segregation in TiO@sub 2@.

2:20pm **SS1-WeA2 Comparison of Physisorption on MgO(100) and TiO@sub 2@(110) Surfaces***, Z. Dohnálek*, *J. Kim, B.D. Kay,* Pacific Northwest National Laboratory

Characterization of oxide surfaces represents one of the current challenges in surface science. In this study we employ physisorption of weakly bound species such as N@sub 2@, O@sub 2@, CH@sub 4@, and Ar to determine the distribution of binding sites on the surfaces of MgO(100) and TiO@sub 2@(110). Cooling of the oxide surfaces to cryogenic temperatures (T < 30K) is critical for conduction such measurements. Both surfaces were extensively studied in the past and represent an ideal platform to correlate surface sites with binding energies of various adsorbates. On MgO(100) only a single temperature programmed desorption (TPD) monolayer feature is observed for all the adsorbates. This is a result of simplicity of unreconstructed MgO(100) surface with checkerboard like arrangement of Mg@super 2+@ and O@super 2-@ ions. TPD spectra observed on TiO@sub 2@(110) are in sharp contrast with those from MgO(100). In this case the surface structure composed of rows of Ti@super 4+@ ions and bridge-bonded oxygens leads to two distinct adsorption geometries. The coverage of the adsorbates in these two geometries is approximately the same and it in agreement with 1:1 ratio of Ti@super 4+@ and bridge-bonded O sites. Typical defects are also probed on both surfaces. On MgO(100) their coverages are determined to be on the order of 15%. Lower coordination of the defect sites results in increased adsorbate binding energies. The effect of oxygen vacancies on the physisorption on TiO@sub 2@(110) is currently being investigated. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

2:40pm **SS1-WeA3 The Oxygen Chemistry on Rutile Titanium Dioxide***, **E.K. Vestergaard***, *E. Wahlström, R. Schaub, J. Matthiesen, F. Besenbacher,* Interdisciplinary Nanoscience Center, Denmark

The detailed understanding of the oxygen chemistry on titanium dioxide is an important issue for chemical and photo-chemical processes on this material. In particular, the detailed route for oxygen vacancy filling through oxygen exposure is important to understand the change of surface reactivity upon re-stoichiometrization. We present STM investigations resolving the atomic-scale details of adsorption, diffusion and reaction of oxygen molecules on the TiO@sub 2@(110) surface. By following the dynamical processes in real time with STM movies, we find that both the diffusion and the reaction between oxygen molecules have activation energies of approximately 0.35 eV and exhibit extremely low attempt frequencies of ~10@super 6@ s@super -1@. These findings are interpreted in a model where charge transfer processes from the TiO@sub 2@ conduction band to the adsorbed oxygen molecules govern the dynamics: Surface oxygen vacancies pin the chemical potential at 0.35 eV from the conduction band, in good agreement with the observed activation energy for diffusion of oxygen molecules.@footnote 1@ The same activation energy is also found for the dynamics of larger oxygen clusters containing three or more atoms. The interaction between such clusters and the bridging oxygen rows on the TiO@sub 2@(110) surface are found to be essential for the understanding of the ability of oxygen to heal the bridging oxygen vacancies. Finally, the presented STM results are discussed in the context of active support materials for Au catalysts. @FootnoteText@ @footnote 1@E. Wahlström et al., Science 303, 511 (2004).

3:00pm **SS1-WeA4 Charge Transfer-Induced Water Splitting on the Rutile TiO@sub 2@(110) Surface***, **R. Schaub***, *E. Wahlström, E.K. Vestergaard, J. Matthiesen, F. Besenbacher,* Interdisciplinary Nanoscience Center, Denmark

In direct contact with water, metal oxides are promising candidates in the search for renewable energy sources through direct photo-splitting of water as suggested by the seminal experiments of Fujishima and Honda@footnote 1@. TiO@sub 2@ is in particular one of the most utilized photo-chemically active systems for waste water treatment. For such photo-chemical processes, surface bound water as well as hydroxyls have been proposed to be the major species which are photo-activated to form hydroxyl radicals responsible for the photochemical activity. By means of scanning tunneling microscopy (STM) we have identified a number of different water-derived adsorbates on the TiO@sub 2@(110) surface, and the details of their formation were revealed from time-resolved STM movies. We find strong evidence that the diffusion of hydroxyls, as well as H@sub 2@O dissociation, is linked to the electronic properties of the substrate in the surface region, in a similar manner to our previous results reported for the interaction of O@sub 2@ molecules with TiO@sub 2@(110)@footnote 2@. Hence, charge transfer from the conduction band of the substrate to adsorbed molecules or reactants is identified as a key factor to understand their physical properties. In other words, chemical reactions can be promoted, not only by a localized "active" site (the traditional approach), but also by the more delocalized conduction band electrons. @FootnoteText@ @footnote 1@ A. Fujishima and K. Honda, Nature 238, 37 (1972).@footnote 2@ E. Wahlström et al., Science 303, 511 (2004).

3:20pm **SS1-WeA5 Photodecomposition of Acetone on TiO@sub 2@(110)***, **M.A. Henderson***, Pacific Northwest National Laboratory

Although acetone is commonly used to evaluate the performance of oxide photocatalysts, little is known about the mechanistic details of its photo-oxidation. This study provides insights into the photodecomposition of adsorbed acetone using the (110) face of rutile TiO@sub 2@ as a model photocatalyst. In the absence of UV light, acetone desorbs from the clean TiO@sub 2@(110) surface without decomposition, exhibiting strong coverage-dependence in its temperature programmed desorption (TPD) peak that shifts from 350 K to below 250 K as the monolayer is populated. Acetone molecules desorbing at 350 K constitute about 0.25 ML and exhibit H/D exchange with surface hydroxyl groups. On the other hand, coadsorbed water displaces about 0.75 ML of the acetone monolayer into physisorbed states, but does not influence the remaining 0.25 ML that constitutes the 350 K TPD peak. These strongly bound acetone molecules are not associated with oxygen vacancies. Virtually no photodecomposition is observed in the absence of gas phase O@sub 2@. Exposure to UV light in gas phase O@sub 2@ results in conversion of acetone to acetate via cleavage of a carbonyl-methyl bond. A similar reaction mechanism occurs in the dark during the coadsorption of acetone and molecular oxygen preadsorbed at oxygen vacancies, suggesting that acetone photodecomposition is facilitated through the excited electron channel (e.g., via reaction with an O@sub 2@@super -@ species) and not through oxidation by valence band holes. Photodesorption measurements reveal that the methyl group is ejected from the surface at 200 K but is retained on the surface at 100 K presumably by conversion into formate based on the absence of likely C@sub 1@ or C@sub 2@ species in TPD. The acetone photodecomposition cross section increases with increasing acetone coverage, but decreases with coadsorbed water. @FootnoteText@ This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

3:40pm **SS1-WeA6 Water Adsorption on the Rutile TiO2(011)-(2x1) Surface***, **A. Klust**, T.J. Beck, U. Diebold,* Tulane University*; C. DiValentin,* Universita' degli Studi di Milano-Bicocca, Italy*; A. Selloni,* Princeton University

Titanium oxide is a promising material for photocatalysis. Previous studies have shown that the photocatalytic activity of rutile TiO@sub 2@ depends dramatically on the surface orientation with the (011) surface being the most active.@footnote 1@ The TiO@sub 2@(011) surface forms a stable (2x1) reconstruction. Based on theoretical modelling and scanning tunneling microscopy (STM) studies, we propose a structural model for this surface. The surface is terminated by one-fold coordinated O atoms (titanyl groups), a feature that distinguishes it from all other known TiO@sub 2@ surfaces. We suggest that the titanyl groups are responsible for the high photocatalytic activity of the TiO@sub 2@(011) surface. Here, we present STM and ultraviolet photoemission (UPS) studies of water adsorption on the TiO@sub 2@(011) surface showing that water adsorb in both molecular and dissociative form at 110 K. First-principles calculations are in agreement with these results and provide detailed information on the structure of the adsorbed molecules. In contrast to the well - known (110) surface@footnote 2@, water dissociation is not mediated by surface defects demonstrating the high chemical activity of the TiO@sub 2@(011)-(2x1) surface. @FootnoteText@ @footnote 1@ G.S. Rohrer in: The Chemical Physics of Surfaces (2001), ed. D.P. Woodruff.@footnote 2@ I.M. Brookes et al. Phys. Rev. Lett. 87 (2001) 266103; R. Schaub et al. Phys. Rev. Lett. 87 (2001) 266104.

4:00pm **SS1-WeA7 Photoexcitation of TiO@sub 2@ and the Chemistry of Electrons and Holes***, **J.T. Yates, Jr.**,* University of Pittsburgh*; O. Diwald,* Technical University of Vienna, Austria*; D. Panayotov, T.L. Thompson,* University of Pittsburgh*; S.D. Walck,* PPG Industries*; T. Berger, E. Knözinger, M. Sterrer,* Technical University of Vienna, Austria **INVITED**

TiO@sub 2@ is a useful photocatalyst for the destruction of trace quantities of organic molecules in the environment. Photoexcitation of TiO@sub 2@ occurs as a result of electron-hole pair excitation by UV radiation with energy above the bandgap (3.0 eV). It has been found that N doping from NH@sub 3@ may be used to lower the photothreshold for TiO@sub 2@ by 0.6 eV, whereas N doping by ion implantation using N@sub 2@@super +@ leads to an increase in the photothreshold energy. Excited electrons in TiO@sub 2@ may be detected by EPR or IR spectroscopy, and hole formation in the valence band region may be detected by EPR as O@super -@ species. Excited electrons are observed to transfer to adsorbed O@sub 2@ to produce the O@sub 2@@super -@ species (superoxide). An adsorbed organic molecule, containing both S and Cl moieties has been shown to accept excited electrons when it is bonded to the surface by the Cl moiety, but not when bound by the S moiety, indicating that charge transfer occurs preferentially into the polyfunctional molecule by means of the more electronegative attachment group.

4:40pm **SS1-WeA9 +ACQ+AHs+Dye Sensitization of the TiO+AEA-Sub 2+AEA- polymorph Anatase (101) Single Crystal Surface by a Series of Dicarboxylated Thiacyanine Dyes+AHs+AH0-***, **N. Ruzycki**, S. Ushiroda, Y. Lu,* Colorado State University*; M.T. Spitler,* ChemMotif, Inc.*; B.A. Parkinson,* Colorado State University

+ACQ-Body +AHs-The dye sensitization of the TiO+AEA-Sub 2+AEA-polymorph anatase (101) is an important system of study because of its application to dye-sensitized solar cells such as the Gr+AEA-um A+AEA-tzel cell. The electrons per photon quantum yields for the dye sensitization of anatase are reported to be higher than those for the rutile polymorph of TiO+AEA-Sub 2+AEA-. The reason that anatase is a better substrate for photovoltaic purposes is yet unknown. The efficiency of solar cells is closely tied to the yield and rate of the electron transfer from the dye molecule to the surface, factors that will be influenced by the geometry of the dye binding and ordering at the surface. Studies that link UHV and electrochemical experiments are a first step towards understanding the mechanism of dye binding to the surface of this material. Dye sensitization of the single crystal anatase (101) surface was studied using a series of dicarboxylated thiacyanine dyes that bind to the surface through the carboxylate group. An ultraviolet (UV) light treatment of the anatase (101) surface, immediately prior to dye adsorption, improves both the reproducibility of dye coverage and the incident photon-to-current efficiencies (IPCE) for sensitization. The UV treatment does not pit or roughen the anatase surface and results in high IPCEs of up to 0.5 percent. The adsorption isotherms and adsorption and desorption kinetics of these dyes were studied. The photocurrent spectra showed features associated with surface-bound dye monomers, dimers and aggregates that could be followed as a function of the dye surface coverage. UHV studies on the single crystal anatase (101) surface were undertaken, including STM, for adsorption of a molecule (bis-isonicotinic acid) that had approximately the same backbone structure and carboxylate group as the dyes in order to elucidate structural models for the dye binding to the surface. +AEA.

5:00pm **SS1-WeA10 Enhanced Photocatalytic Activity in Fe@sub 2@O@sub 3@/Cr@sub 2@O@sub 3@ Epitaxial Heterojunctions***, **J.R. Williams**, S.A. Chambers, M.A. Henderson,* Pacific Northwest National Laboratory

The heterogeneous photocatalytic activity may be enhanced by the creation of an oxide-oxide heterojunction where the band alignment is such that photoexcited electron-hole pairs tend to separate at the interface, resulting in enhanced charge carrier lifetimes. Here we show that epitaxial heterojunctions of Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@ do indeed exhibit enhanced photocatalytic activity relative to either pure material. The dependence of the enhancement on the heterojunction thickness will be discussed, as well as the wavelength dependence. The heterojunctions were grown on @alpha@-Al@sub 2@O@sub 3@ substrates by Oxygen Plasma Assisted Molecular Beam Epitaxy (OPA-MBE). Characterization by XPS and all photocatalysis experiments are performed in situ after growth with no air exposure at any time. Photocatalytic activity is measured by the extent of decomposition of trimethylacetic acid (TMA) adsorbed on the surface using a quadrupole mass spectrometer, XPS, and a Hg arc lamp with various filters as the excitation source. Specifically we have observed a factor of ~ 2-3 increase in photocatalytic activity for this type of heterojunction surface as compared to the same surface of either pure material.

Surface Science
Room 210C - Session SS2-WeA
Surface Collision Dynamics

Moderator: K.P. Giapis, California Institute of Technology

2:00pm **SS2-WeA1 Atomic-Scale Analysis of the SiH@sub 3@ Surface Reactivity During Plasma Deposition of Amorphous Silicon Thin Films***, **M.S. Valipa**, E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition are used widely in the fabrication of solar cells and flat panel displays. The dominant precursor for deposition of device-quality a-Si:H films is the SiH@sub 3@ radical. Development of systematic strategies for depositing a-Si:H films with desirable properties requires a fundamental understanding of surface reactions of the SiH@sub 3@ radical leading to a-Si:H growth and H incorporation. This presentation focuses on detailed atomic-scale analysis of the surface reactions of SiH@sub 3@ using molecular-dynamics simulations of repeated impingement of SiH@sub 3@ radicals on growth surfaces of smooth a-Si:H films. The corresponding surface reaction probability, @beta@, is determined over the temperature (T) range 475-800 K. SiH@sub 3@ can either incorporate into the film by adsorbing onto a dangling bond or inserting into Si-Si bonds (sticking), or abstract surface H through Eley-Rideal (ER) or Langmuir-Hinshelwood (LH) pathways to produce SiH@sub 4@ gas, or react with another surface SiH@sub 3@ to desorb as Si@sub 2@H@sub 6@ (recombination), or leave the film by reflection or desorption. The overall @beta@ (sticking + recombination) is almost constant over the T range studied, as are the probabilities for sticking and recombination, s and @gamma@, respectively. Energetic analysis shows that SiH@sub 3@ adsorption and insertion and ER abstraction are barrierless processes, which explains the measured T independence of @beta@. LH abstraction is activated at high T, but competes with Si@sub 2@H@sub 6@ formation, yielding a T-independent @gamma@. Also, LH abstraction leads to H elimination from a-Si:H during growth and explains the T dependence of H content in the a-Si:H film.

2:20pm **SS2-WeA2 Adsorption Induced Phase Separation followed in Real Time by High-pressure Scanning Tunneling Microscopy**, ***J. Knudsen***, *R.T. Vang, E.K. Vestergaard, F. Besenbacher,* University of Aarhus, Denmark

The validity of surface science experiments as an efficient tool in catalysis research is often questioned due to the enormous difference in pressure conditions. For single metal systems the issue is most often concerned with the equivalence between adsorption phases obtained under low pressure and low temperature versus high pressure and high temperature phases. But for the case of more complex model systems such as bimetallic alloys the stability of the model catalyst becomes an additional important factor. We have developed a high-pressure fast-scanning STM which serves as an ideal tool for studies of high pressure induced morphological and structural changes in real time by the acquisition of STM movies. In this way we have been able to describe in great detail a CO induced phase separation of a Au/Ni(111) surface alloy. The STM movies reveal how a removal of nickel atoms from the topmost layer of the alloy surface is nucleated at the step edges of the surface. The gold atoms are left behind on the surface, and small gold clusters are formed in the wake of the moving step edge. Based on these experimental findings we propose a model, in which nickel atoms are removed by the formations of nickel carbonyls; a reaction that is well known from studies of clean nickel surfaces. Finally, we present recent studies of the stability of a Cu/Pt(111) surface alloy under high CO pressures. Exposure of the Cu/Pt(111) surface alloy to CO leads to the formation of clusters on the surface. The atomic details of this adsorbate-induced structural change of the Cu/Pt(111) alloy are currently being investigated.

2:40pm **SS2-WeA3 Quantum State Resolved Studies of Gas/Surface Reaction Dynamics**, ***R.D. Beck***, Ecole Polytechnique Federale de Lausanne (EPF), Switzerland **INVITED**

The dissociation of methane on a nickel catalyst is a key step in steam reforming of natural gas for hydrogen production. Despite substantial effort in both experiment and theory, there is still no atomic scale description of this important gas-surface reaction. To elucidate its dynamics, we have performed quantum state resolved studies of vibrationally excited methane reacting on the Ni(100) surface using pulsed laser and molecular beam techniques. We observed up to a factor of 5 greater reaction probability for methane-d2 with two quanta of excitation in one C-H bond versus a nearly isoenergetic state with one quanta in each of two C-H bonds. For CH4, stimulated Raman pumping is used to probe the reactivity of the totally symmetric C-H stretch vibration for comparison with reactivity of CH4 excited to the infrared active antisymmetric C-H stretch vibration. The observed reactivities point to a transition state structure which has one of the C-H bonds significantly elongated. Our results also clearly exclude the possibility of statistical models correctly describing the mechanism of this process and emphasize the importance of full-dimensional calculations of the reaction dynamics.

3:20pm **SS2-WeA5 Gas-Surface Reaction Dynamics at the Inorganic-Organic Interface**, ***A. Dube***, *P.F. Ma, A.S. Killampalli, M. Sharma, J.R. Engstrom,* Cornell University

Inorganic-organic interfaces play an important role in a number of technologies. Much of the work to date in the area of gas-surface reaction dynamics has involved study of the reaction of small organic molecules with transition metal surfaces. Here, we have chosen to examine the inverse problem: the reaction of coordination compounds of transition metals with model organic surfaces using supersonic molecular beam techniques. Such reactions are the first key step to barrier formation on organic surfaces, and they may result in a superior method for the formation of contacts to molecular electronics. In the work we report here we examine explicitly the reaction of Ti- and Ta- containing coordination compounds with a variety of self-assembled monolayers (SAMs) possessing different terminal endgroups (e.g.,-CH@sub 3@,-OH, -NH@sub 2@,-COOH), using both HX-R-SiCl@sub 3@/SiO@sub 2@ and HX-R-SH/Au based SAM chemistries. For example, for the reaction of Ti[N(CH@sub 3@)@sub 2@]@sub 4@ and for molecular kinetic energies E@sub i@ = 0.5-2.0 eV, we find that the reaction probability on -OH and -NH@sub 2@ terminated R-SiCl@sub 3@/SiO@sub 2@ type SAMs passes through a minimum, near E@sub i@ ~ 1 eV. Since we have shown in other work that penetration of the SAM by the coordination compound is possible, these results suggest that penetration is enhanced at sufficiently high E@sub i@. On the other hand, variation of both the substrate temperature and the angle of incidence indicates that reaction with these two terminal endgroups follows a trapping-mediated chemisorption channel. In selected cases we also make comparison to results from ab initio quantum chemistry calculations of the potential energy surface. For example, these calculations are consistent with a barrier near the vacuum level for the reaction on -OH terminated SAMs, which we observe experimentally, yet they suggest that reaction with an isolated -NH@sub2@ may be activated by as much as 15 kcal-mol@super -1@.

3:40pm **SS2-WeA6 Site-Selective Abstraction in the Reaction of 5- to 20-eV O@super +@ with a Self-Assembled Monolayer**, ***X. Qin***, *T.D. Tzvetkov, D.C. Jacobs,* University of Notre Dame*; D. Lee, L. Yu,* University of Chicago

The reaction of hyperthermal (5-20 eV) O@super +@ with alkanethiolate self-assembled monlayers (SAM) is studied under UHV conditions. To learn about the site-specificity to hydrogen abstraction in this system, we deposit SAM layers for which the hydrogen atoms located on the C-12, C-11, or C-10 positions of 1-dodcanethiol are substituted with deuterium atoms. By comparing the yields of OH to OD emerging from these three isotopomers, we find that hyperthermal O@super +@ initially abstracts only H(D)-atoms bound to the top two carbon atoms within the SAM layer. Continued bombardment with O@super +@ ions significantly disorders the structure of the SAM.

4:00pm **SS2-WeA7 Current Research and Development Topics on Gas Cluster Ion Beam Processes**, ***I. Yamada***, University of Hyogo, Japan**INVITED**

It has been 15 years now since the idea of the gas cluster ion beam (GCIB) process first came up, but the interest in GCIB process has increased only recently, driven by the nano-technology program, especially in Japan. This ion beam process uses a beam of ions consisting of clusters of a few hundreds to thousands of atoms generated from gaseous materials. The impact of these accelerated cluster ions with the surface produces a low energy bombardment at very high density. The cluster-surface collisions were found non-linear effects and to have unique characteristics which were found to be useful for applications in novel surface processing. These characteristics include surface effects such as shallow implantation, lateral sputtering, cleaning and smoothing, as well as low temperature thin film formation. This paper reviews the current fundamental research related to the GCIB-surface interactions as well as their applications in modern magnetic, optical and semiconductor device fabrications. These presently include: (i). IC Back End of the Line (BEOL) materials processing, (ii). surface smoothing of metals, dielectrics, superconductors, and diamond films for optical and magnetic devices, (iii). selective smoothing of SOI, SiC and compound semiconductor films and (iv). high quality thin multi-layer film deposition for reliable and durable optical filters.

Science of Semiconductor White Light Topical Conference
Room 304B - Session WL+MS-WeA

Science of Semiconductor White Light II

Moderator: K.H.A. Bogart, Sandia National Laboratories

2:00pm **WL+MS-WeA1 Material and Device Challenges of Deep UV Emitters**, ***M.H. Crawford***, *A.A. Allerman, A.J. Fischer, K.H.A. Bogart, S.R. Lee, W.W. Chow,* Sandia National Laboratories **INVITED**

One of the new frontiers of light emitting diode research is the application of wide bandgap AlGaN alloys to achieve electroluminescence at 300 nm and shorter wavelengths. While most near-UV (380-400 nm) LEDs employ InGaN quantum well structures with GaN barriers, reaching deep UV wavelengths requires the growth of AlGaN alloys with aluminum concentrations of 50% and higher. In this presentation, we will review the present status of LED technology in the deep UV range and will discuss in detail the material and device challenges for achieving high performance devices. We will present data on LEDs that are grown by metal-organic vapor-phase epitaxy and employ flip-chip device geometries. These devices have yielded > 1 mW output powers in the 275-290 nm range under DC current operation. Critical device issues that will be discussed include performance under pulsed current injection, device lifetimes and an evaluation of the origins of deep level emission in the electroluminescence spectra. Electroluminescence at wavelengths shorter than 250 nm will be presented, and limitations of short wavelength performance will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This work is supported by DARPA under the SUVOS program.

2:40pm **WL+MS-WeA3 Interfaces in White Light-Emitting Structures**, ***P.H. Holloway***, University of Florida **INVITED**

Solid state devices have the promise to revolutionize the generation of white light. Solid state lighting has the potential to increase the efficiency of converting electricity to light by factors of two or more. The solid state structures are robust and hint at lifetimes of thousands of hours. Interfaces in these devices will play an important role in the fulfillment or collapse of this promise. The best performance to date has been achieved with light emitted from GaN-based LEDs which contribute a blue component to the emitted light, while simultaneously photo-pumping one or more phosphors which luminescence to provide a color spectrum with a good color rendering index. Critical interfaces in these structures range from the interfaces between the epitaxial layers, to the metal-semiconductor interfaces for ohmic contacts, to the matix-phosphor interface for light scattering and quenching luminescence. Our knowledge about these types of interfaces will be illustrated using examples of interfacial characterization and reactions, and the need for new understanding will be illustrated.

3:20pm **WL+MS-WeA5 Ohmic Contacts to (Al)GaN Semiconductors for Light Emitters***, **I. Adesida**,* University of Illinois at Urbana-Champaign **INVITED**

The direct bandgap of GaN-based semiconductors have made them attractive materials for the realization of a wide range of optoelectronic devices. Examples of devices that are either commercially available or have been demonstrated include short wavelength light emitting diodes (LEDs), solar blind detectors, and laser diodes which have applications in white light illumination, bio-chemical agent sensing, solar UV detection, missile detection, flame and heat sensing, ozone monitoring, and remote sensing. Materials growth and device processing are still critical issues in terms of obtaining highly efficient GaN-based optoelectronic devices. The realization of highly reliable, thermally stable, low resistance ohmic contacts to both n-type and p-type GaN-based semiconductors is essential. To date, the formation of contacts to AlGaN with high Al concentration remain a challenge for various reasons. In this paper, we will describe our work on ohmic contact formation on both n- type and p-type AlGaN of various Al concentrations. Results on n-type contact formation using various metallization schemes will be presented. Contact formation to p-type AlGaN using Pd-based metallization schemes will be presented. Issues of thermal stability of these contacts will be discussed. The efficacy of various surface treatment schemes for GaN and AlGaN to improve the ohmic performance of the contacts will be discussed. Comprehensive studies are being performed to compare the effects of various surface treatment schemes which include both plasma and wet processes on the electrical and material characteristics of GaN and AlGaN semiconductors. Further, the mechanism of formation of ohmic contacts in these semiconductors will be discussed.

4:00pm **WL+MS-WeA7 Passivation and Processing-Induced Changes in GaN/Insulator Interfaces***, **R.J. Nemanich**, T.E. Cook, Jr., C.C. Fulton, W.J. Mecouch, R.F. Davis, G. Lucovsky,* NC State University **INVITED**

Passivation of GaN and AlGaN surfaces is now a critical limitation in electronic device fabrication. The band relations of various dielectrics on III-nitrides are just being established, and some interfaces show significant process induced variations. The characteristics of clean n- and p-type GaN (0001) surfaces and the interface between this surface and SiO2, Si3N4, and HfO2 have been investigated. Layers of SiO2, Si3N4, or HfO2 were carefully deposited to limit the reaction between the dielectric and the clean GaN surfaces. After stepwise deposition, the electronic states were measured with x-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). A valence band offset (VBO) of 2.0 eV with a conduction band offset (CBO) of 3.6 eV was determined for the GaN/SiO2 interface. For the GaN/Si3N4 interface, type II band alignment was observed with a VBO of 0.5 eV with a CBO of 2.4 eV, which differs substantially from prior reports. We suggest that the differences are related to the level of oxygen incorporated at the interface. A VBO of 0.4 eV with a CBO of 2.0 eV was determined for the GaN/HfO2 interface. An instability was observed in the HfO2 film, with energy bands shifting ~0.5 eV during a 650Â°C densification anneal. The deduced band alignments were compared to the predictions of the electron affinity model and deviations were attributed to a change of the interface dipole. The largest deviation was observed for the oxide layers. It was noted that the existence of Ga-O bonding at the heterojunction can significantly affect the interface dipole, and consequently the band alignment in relation to the GaN.

4:40pm **WL+MS-WeA9 Emissivity-Correcting Pyrometry for Group-III Nitride MOCVD***, **J.R. Creighton**, C.C. Mitchell,* Sandia National Laboratories **INVITED**

Accurate temperature measurement during group-III nitride MOCVD is very difficult due to the broad spectral transparency of the substrates and epitaxial layers. In fact, there is no readily available method that measures the true surface temperature during deposition. We have developed a pyrometer that operates near the high-temperature bandgap of GaN, thus solving the transparency problem once a ~1 micron thick GaN epilayer has been established. At typical GaN MOCVD conditions the RMS temperature noise of the system is <0.1°C. By simultaneously measuring the reflectance, we can also correct for emissivity changes when films of differing optical properties (e.g. AlGaN) are deposited on the GaN template. By employing the virtual interface method, the reflectance measurement can also be used to monitor growth rates and compute optical properties of the thin films. Using this method we have measured the high temperature optical constants of GaN at the effective pyrometer wavelength (405 nm). Near 1000°C, the imaginary part (k) of the GaN refractive index is ~0.2, thus demonstrating that the epilayer is opaque. Small artifacts (due to stray light) in the emissivity-correction method are often observed, leading to residual oscillations in the corrected temperature. For our new nitride pyrometer the residual temperature oscillations are typically <3°C in amplitude when growing AlN/GaN heterostructures. Through proper calibration experiments, the nature of the error can be understood and quantitatively eliminated. We will also report on our recent efforts to extend this nitride pyrometer technology to multiwafer MOCVD reactors. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.).

Surface Science
Room 210B - Session SS1-ThM
Metal Oxide and Clusters III: Supported Cluster Formation and Reactivity

Moderator: G.S. Hwang, The University of Texas at Austin

8:20am **SS1-ThM1 Decomposition of Dimethyl Methylphosphonate on TiO@sub2@(110)-Supported Ni Clusters of Different Sizes***, **D.A. Chen**, S. Ma,* University of South Carolina*; J. Zhou,* Oak Ridge National Laboratory

The thermal decomposition of dimethyl methylphosphonate (DMMP) on Ni clusters deposited on TiO@sub2@(110) has been studied in ultrahigh vacuum by TPD and XPS. Ni cluster sizes were characterized by STM; the small Ni clusters (5.0±0.8 nm diameter, 0.9±0.2 nm height) were deposited at room temperature while the large clusters (8.8±1.4 nm diameter, 2.3±0.5 nm height) were prepared by room temperature deposition followed by annealing to 850 K. TPD experiments show that CO and H@sub2@ were the major gaseous products evolved from the decomposition of DMMP, and molecular DMMP and methane desorption were also observed. The product yields for CO and H@sub2@ were higher for reaction on the small Ni clusters. Furthermore, XPS experiments demonstrate that the small Ni surfaces decompose a greater fraction of DMMP at room temperature. The loss of activity for the large annealed clusters is not caused by a reduction in surface area, which does not change substantially before and after annealing. Since CO adsorption studies suggest that the loss of activity cannot be completely due to a decrease in surface defects upon annealing, we propose that a TiO@subx@ moiety is responsible for blocking active sites on the annealed Ni surfaces. Low ion scattering studies show that the Ni clusters are not completely encapsulated after heating to 850 K, but these experiments are also consistent with partial encapsulation. Although DMMP decomposes on TiO@sub2@ to produce gaseous methyl radicals, methane and H@sub2@, the activity of the substrate surface itself appears to be quenched in the presence of the Ni clusters. However, the TiO@sub2@ support plays a significant role in providing a source of oxygen for the recombination of atomic carbon on Ni to form CO, which desorbs above 800 K.

8:40am **SS1-ThM2 Nucleation and Growth of 1B Metals on Rutile TiO2(110): Role of Oxygen Vacancies***, **D. Pillay**, G.S. Hwang,* The University of Texas at Austin

Oxide supported metal nanoparticles exhibit distinctly different chemical and physical properties from their bulk counter parts. The unique properties are greatly determined by their size and shape. Tailoring the structural properties with atomic scale precision will therefore offer great opportunities to open up a range of novel chemical, biological, and electronic applications. Due to the complexity of oxide-metal interactions, many fundamental aspects of metal particle nucleation and growth on an oxide are not well understood. We have investigated the nucleation and growth of 1B metals (Cu, Ag, Au) on a rutile TiO2(110) surface using density functional theory slab calculations. Our results clearly demonstrate that Au shows a distinctly different growth behavior from Ag and Cu. In this talk, we will present i) diffusion, nucleation, and early stage of growth of 1B metals on reduced TiO2(110) and ii) role of oxygen vacancies in the metal particle growth. Also, we will discuss the underlying reasons for sintering enhancement upon O2 exposure.

9:00am **SS1-ThM3 Cluster Size and Support Effects on Activity in Supported Gold and Iridium Catalysts***, S. Lee, C. Fan, T. Wu, W. Kaden, **S.L. Anderson**,* University of Utah **INVITED**

Size-selected model catalysts are prepared by deposition of mass-selected gold and iridium cluster ions on single crystal TiO@sub 2@ and thin film Al@sub2@O@sub 3@. Physical properties and adsorbate binding to the resulting samples is probed by a combination of XPS and ion-scattering (ISS). Chemical activity is probed by a combination of temperature-programmed desorption and constant temperature pulse dosing mass spectrometry. CO oxidation on Au@sub n@/TiO@sub 2@ is found to be very strongly dependent on deposited cluster size, with activity turning on at Au@sub 3@, and varying with size for larger clusters. The activity appears to be correlated with changes in the binding of CO from atop gold to peripheral sites associated with the clusters. Comparison of samples prepared by deposition over a wide temperature range suggests that substantial sintering occurs only at temperatures well above room temperaure. Reactions of hydrazine and ammonia on Ir@sub n@/Al@sub2@O@sub 3@, and sintering behavior in this system will also be discussed.

9:40am **SS1-ThM5 Fullerene Surfaces as Templates for Cluster Formation: The Interaction with Silicon and Gold***, **P. Reinke**,* University of Virginia*; H. Kroeger,* Universitaet Goettingen, Germany*; M. Buettner, P. Oelhafen,* Universitaet Basel, Switzerland

Clusters made from different elements are envisaged as building blocks for nanoelectronic devices. The properties of small clusters (@<@100 atoms) exhibit a strong size dependence which allows to tune their properties but places considerable demands on the synthesis of size-selected cluster arrays. The present investigation explores a novel path to the synthesis of size-selected clusters exploiting the strong corrugation and wide range of adsorption sites on the C@sub 60@ surface. Si and Au are the first elements investigated and the possibility to form arrays and network structures will be explored in the future. Amorphous Si (a-Si) and Au were deposited on a fullerene surface and the sequential evolution of the surface and the electronic properties of the interface were observed in-situ by photoelectron spectroscopy (PES) in the ultraviolet and x-ray regime. The growth of the Si on the C@sub 60@ surface begins with the formation of clusters, and analysis of the Si2p core level indicates that they are surrounded by carbon atoms and located interstitially between the C@sub 60@ molecules. As the growth continues the clusters coalesce and an a-Si overlayer forms. The interface contains no SiC covalent bonds and the electronic properties of this sharp interface are determined from the PES data. In contrast, the growth of the Au overlayer begins with the formation of islands, followed by a Vollmer-Weber type growth. The analysis of the core level and valence band spectra yields a wealth of information on the cluster size, electronic structure of the clusters and the interface. A model to describe this behavior will be discussed with special attention to the suitability of the system for cluster array and network formation, and with respect to the future use of highly corrugated surfaces of macromolecule solids to aid these self organization processes.

10:20am **SS1-ThM7 The Role of Defects in the Nucleation, Structure, and Stability of Gold Clusters on Titania***, **W.T. Wallace**, M.-S. Chen, B.K. Min, K.K. Gath, D.W. Goodman,* Texas A&M University

The discovery that Au clusters dispersed on certain metal oxides are efficient catalysts for a variety of low-temperature reactions has stimulated extensive study with the goal of developing a new generation of superior, Au-based catalysts. In this study, the interaction of Au with titania, a commonly used industrial support, has been addressed. Titania, as a 3-D cluster, or a titanium cation, introduced as a heterogeneous defect into a silica thin film, acts as a nucleation site for Au clusters, leading to an enhanced cluster density. Furthermore, both types of defects inhibit Au cluster sintering under reaction pressures and temperatures, thereby circumventing a serious limitation of the typical nanostructured Au catalysts. The growth mode of Au deposited onto titania thin films grown on Mo(112) illustrates the crucial role of surface structure on the Au morphology. On titania films grown on Mo(100), Au forms 3-D clusters when annealed, whereas on a highly defective titania surface grown on Mo(112), Au grows layer-by-layer, forming a thin, ordered film that exhibits exceptional catalytic activity toward CO oxidation.

10:40am **SS1-ThM8 Interaction of CO, Au, and O on Ru(0001)***, **Q. Wu**, J. Hrbek,* Brookhaven National Laboratory

The coadsorption of O, Au, and CO is studied on the Ru(0001) surface using temperature programmed desorption, Auger electron spectroscopy, and low energy electron diffraction. For low oxygen coverage (O(2x1) or @theta@@sub O@ = 0.5 ML), Au is found to compress the surface oxygen, and contributes to two first-order-like desorption peaks of O@sub 2@ (e.g. ~1150K and ~1200K). The double-peak structure of O@sub 2@ desorption is also observed when Au compresses the "O-rich" Ru(0001) surface (O(1x1) or @theta@@sub O@ ~1 ML excluding subsurface oxygen); the desorption of subsurface oxygen occurs at ~1050K. Desorption is a dynamic process: after subsurface O desorption, compressed surface oxygen starts to desorb and gold spreads on the Ru surface. Au desorption (0.5 ML to 5 ML) from the oxygen modified Ru surface (both O(2x1) and O(1x1)) is consistent with the presence of 3D Au islands. The majority of CO coadsorbed on Au/O/Ru(0001) surface desorbs at low temperatures around 200K; a small fraction reacts with the compressed oxygen to form CO@sub 2@ that desorbs at ~300K.

11:00am **SS1-ThM9 Adsorption and Desorption of Propylene and Ethylene on Au/TiO@SUB 2@**, ***Y. Yang**, M.M. Sushchikh, E.W. McFarland,* University of California, Santa Barbara

TiO@sub 2@ supported Au nanoclusters are of interest both as olefin epoxidation catalysts as well as a more general high activity partial oxidation platform. Four different TiO@sub 2@ (110) surfaces were prepared; ideal, fully oxidized, and defected by 0.1% , 1% and 10% surface area sputtering. Identical exposures (270 K (1%) and 300 K (10%)) while the TiO@sub 2@ related peak remains at 150 K. We propose that Au deposited on a sputtered surface is immobilized at defect sites and that with increased sputtering time there is a decrease in the cluster size. The propylene metal interaction is increased in energy as the cluster size decreases. Similar behavior is observed with ethylene desorption.

11:20am **SS1-ThM10 Chemistry of Sulfur Compounds on Au(111)-Supported Mo Nanoparticles.**, ***D.V. Potapenko**,* Brookhaven National Laboratory*; J.M. Horn, M.G. White,* BNL and SUNY at Stony Brook

We are using the reconstructed (21 x @sr@3)-Au(111) surface as a template and inert support for depositing Mo nanoparticles for subsequent reactivity studies of desulfurization and the formation of Mo sulfide nanoparticles. Bulk molybdenum sulfide is the basis for commercial hydrodesulfurization (HDS) catalysts and this work is focused on exploring the modification of activity for nanostructured Mo and molybdenum sulfide on various supports. Nanoparticles of Mo were prepared on the Au(111) substrate by two methods: physical vapor deposition of Mo and chemical vapor deposition through the Mo(CO)@sub 6@ precursor. STM studies have shown that Mo nanoparticles are thermodynamically unstable on the Au(111) surface and that gold encapsulates Mo at temperatures > 300 K. It follows from TPD/AES experiments that bare Mo nanoparticles are very reactive: they cause complete dissociation of all the S-containing compounds tried and H@sub 2@ was the only major desorption product observed. Au-encapsulated Mo nanoparticles, on the other hand, are much less reactive. They do not chemically interact with thiophene (C@sub 4@H@sub 4@S). Surprisingly, Au-encapsulated Mo nanoparticles react with both H@sub 2@S and CH@sub 3@SH. The latter compound in this case dissociates only partially, causing S deposition and desorption of CH@sub 4@. We believe that interaction of X-SH compounds with Au-encapsulated Mo nanoparticles proceeds through intermediacy of surface gold thiolates.

11:40am **SS1-ThM11 Metal Oxide Nanowires: How Nano-Electronics Can Contribute to Catalysis**, ***A.A. Kolmakov**, Y. Lilach, M. Moskovits,* University of California, Santa Barbara

We tested the performance of individual metal oxide single crystal nanowires and nanobelts as catalysts and gas sensors operating in high vacuum and under "real world" reaction conditions. We showed that when nanowire radius is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire alters the bulk electron density inside the nanowire what can be sensitively monitored via changes in the conductivity of the nanowire. When nanowire is configured as a field effect transistor the availability of free electrons in the bulk for redox surface reactions can be controlled by the gate thus reactivity (sensitivity) and selectivity of the nanowire surface can be tuned electronically. In vivo conductometric measurements on individual nanowire during its surface doping with catalytic particles manifest the drastic enhance of the reactivity/selectivity of this catalyst (sensor) due to selective adsorption and spillover effect.

Surface Science
Room 210C - Session SS2-ThM
Tribology, Adhesion, and Friction

Moderator: I.L. Singer, Naval Research Laboratory

8:40am **SS2-ThM2 Advanced Adhesion Test Methods for Semiconductor Interconnect Film**, ***A.K. Sikder**, N. Gitis, M. Vinogradov,* Center for Tribology, Inc.

For faster signal propagation in integrated circuits, new materials with lower dielectric constant (low-k) values are required with copper metal lines. Low-k materials possess many challenges due to their poor mechanical integrity and weak adhesion to other interconnects, so it is important to characterize their adhesion behavior. There are numerous techniques known for adhesion and delamination testing of coatings, some of the most common being a tape test, stud-pull test, scratch test and an indentation test. Each of them has its advantages, but neither one is universally effective for soft to hard, ultra-thin to thick films. The new testing technology, based on multiple sensors coupled with servo-control of forces and displacements, has been developed to fill this void. A novel technology for scratch testing has been developed in order to evaluate the tribo-mechanical behavior of interconnect thin films, where an indenter moves in both vertical (loading) and horizontal (sliding) directions, while acoustic emission and electrical resistance sensors allow for detection of the initiation of fracture, and the scratch pattern indicates the type of failure. The impression left by scratch testing is then observed using scanning probe and optical microscopy, integrated into the instrument mod. UNMT. Scratch testing on various interconnect blanket and patterned, single and multilayered, polished and unpolished film is presented. Adhesion and delamination characteristics are discussed with respect to the intrinsic properties of the different interconnect films (low-k, copper and tantalum) and their surface roughness. Their effective testing in the stack of the films is complimented by frictional and acoustic measurements. The multi-sensing technology allowed for comprehensive characterization of the scratch, adhesion and durability of thin coatings.

9:00am **SS2-ThM3 Light vs. Heavy Diamond: an Investigation of the Fundamental Origins of Friction**, ***R.J. Cannara**, R.W. Carpick,* University of Wisconsin-Madison

Mechanisms of friction include wear, bond-breaking and surface chemistry, molecular deformation, electronic dissipation, and vibrational excitations (or phonons). Resolving the individual contribution of each of these mechanisms poses a great challenge. To overcome this obstacle and isolate the role of phonons in frictional energy dissipation, we compare insulating crystals that are identical, except for having different isotopic concentration. We report adhesion, as well as load- and temperature-dependent nano-scale friction measurements, for a tungsten carbide-coated Si tip on the hydrogen-terminated (111) surfaces of three single-crystal synthetic Type IIa diamonds. Each of the specimens is composed of a different bulk mixture of @super 12@C and @super 13@C. Varying the average mass and isotopic disorder in diamond strongly influences its phonon band structure and thermal properties. For example, previous work has revealed that both phonon lifetimes and thermal diffusivity of diamond increase with isotopic purification. Moreover, its thermal diffusivity is dramatically enhanced at low temperatures (down to ~100 K). All of these phonon properties determine the probability that atomic vibrations (initially created by slip processes during sliding) will reduce frictional energy dissipation by aiding subsequent slip events. We discuss isotope, or phonon, contributions to atomic-scale friction measurements performed in nitrogen and ultra-high vacuum at different temperatures. In addition, we present evidence for structural interfacial effects that lead to negative differential friction behavior.

9:40am **SS2-ThM5 Frictional Forces and Amontons' Law: From the Molecular to the Macroscopic Scale**, ***U. Landman**, J. Gao, W.D. Luedtke,* Georgia Institute of Technology **INVITED**

Amontons' law, which was already known to Leonardo da Vinci, states that the friction force is directly proportional to the (normal) applied load, with a constant of proportionality - the friction coefficient - that is constant and independent of the contact area, the surface roughness and the sliding velocity. No theory has yet satisfacorily explained this surprisingly general law, all attempts being model or system dependent. On the basis of large-scale molecular dynamics simulations pertaining to lubricated adhesive and non-adhesive junctions, with morphologically rough (as well as crystallographically flat) confining solid surfaces, and in conjunction with recent experiments, we show that the local energy-dissipation mechanisms are not 'mechanical', as assumed in most models, but â?othermodynamicâ?□ in nature. We show that a local analysis of the simulation results, based on division of the system into small cells, leads to a natural description in terms of the Weibull distribution. For the dynamic. non-equilibrium, energy-dissipating process that we study, this long-tail distribution serves a similar purpose as the Boltzmann distribution for classical systems at equilibrium. While Amontons' law does not hold on the local scale, it is recovered on the global scale, with the spatio-temporal averaging utilizing the Weibull distribtion of the local friction forces. Interestingly, the concept of "area of contact", often used in frictional studies, does not enter into our analysis. J. Gao, W.D. Luedtke, D. Gourdon, M Ruths, J.N. Israelachvili, U. Landman, Feature Article, in J. Phys. Chem. B 108, 3480 (2004).

10:20am **SS2-ThM7 Activation of SiC Surface for Vapor Phase Lubrication by Chemical Vapor Deposition of Fe***, D. Kim, A.J. Gellman,* Carnegie Mellon University

Vapor phase lubrication (VPL) has been proposed as a method for lubricating high temperature engines. During VPL, lubricants such as tricresylphosphate (TCP), (CH@sub 3@-C@sub 6@H@sub 4@O)@sub 3@P=O, are delivered through the vapor phase to high temperature engine components where they react to deposit a thin, solid, lubricating film. Although ceramics such as SiC are desirable materials for high temperature applications their surfaces are unreactive for the decomposition of TCP and thus not amenable to vapor phase lubrication. As a means of activating the SiC surface for TCP decomposition we have used chemical vapor deposition of Fe from Fe(CO)@sub 5@. Modification the SiC surface by the presence of Fe accelerates subsequent decomposition of TCP and deposition of P and C on the surface. m-TCP decomposes more readily in the temperature range of 300 K - 500 K on Fe-coated SiC surfaces than on SiC surfaces. The C and P deposition rates depend on the thickness of the Fe film and are further enhanced by oxidation of the Fe. This work provides a proof-of-concept demonstration of the feasibility of using vapor phase to lubricate ceramics.

10:40am **SS2-ThM8 In Situ Studies of Interfacial Rheology of MoS2 and Most Solid Lubricating Coatings***, G.Y. Lee, I.L. Singer,* Naval Research Laboratory*; **K.J. Wahl,*** Naval Research Laboratory, US

Materials properties (e.g. composition, microstructure, and mechanics) of both solid lubricant coatings and their interfacial transfer films have long been recognized as important to tribological performance. These properties are generally evaluated ex situ, before and after sliding have occurred. However, in situ observations of contacts have shown that interfacial rheology - the deformation and flow of matter within the contact - plays a significant role in controlling friction, wear and endurance of solid lubricants. In this paper, we will present real-time observations of interfacial rheology of MoS2 and MoST@footnote 1@ (Ti-Mo-S) coatings using in situ tribometery. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 and 20% titanium. Reciprocating tests were performed in both dry (<1%) and ambient air (45-60% RH) at 1-4 mm/s and under 1.1 GPa mean contact stress. The interface rheology was studied quantitatively using optical microscopy techniques. Transfer film buildup and depletion were monitored quantitatively using interference fringes, while interfacial dynamics (locus of sliding, stability, and strain rate) were evaluated through video microscopy. The interfacial rheology of MoS2 coatings was strongly influenced by environment (dry vs. humid). In contrast, interfacial rheology of MoST coatings was far less sensitive to humidity, but was strongly influenced by evolution of wear track surface composition and morphology. We will demonstrate how these quantitative measures of interfacial rheology can be used to help us interpret how transfer films influence friction, wear and endurance of MoS2-based solid lubricant coatings. @FootnoteText@ @footnote 1@ D.G. Teer, Wear 251 (2001) 1068-1074.

11:00am **SS2-ThM9 Self-Assembled Monolayers: The Origin of Molecular Level Friction***, **R.C. Major**, X.-Y. Zhu,* University of Minnesota*; J.E. Houston,* Sandia National Laboratories

Functionalized self-assembled monolayers (SAMs) are being used in a broad spectrum of disciplines to control the chemical and physical properties of surfaces at the molecular level. Despite a large number of studies, current understanding of the mechanical properties of these functional SAMs is rather incomplete. This arises in part because of the difficulty in quantitatively measuring adhesion and friction forces on the molecular level, and due to the non-trivial task of preparing well-ordered, functionalized thiol monolayers containing reactive endgroups (e.g. HS-(CH@sub 2@)@sub n@-COOH vs HS-(CH@sub 2@)@sub n@-CH@sub 3@) on Au(111) substrates; the latter has often been overlooked in the past literature. Here we report a quantitative study on the tribological properties of functionalized SAMs on Au(111) using Interfacial Force Microscopy (IFM). We show the intimate relationship of tribological properties with the chemical state of the SAM. For example, in the case of -COOH terminated SAMs, we observed a dramatic reversible change in friction response corresponding to the protonated and deprotonated state of the -COOH groups. This frictional response showed an interesting dependence on the conformation and length of the alkyl chains. Microscopic models correlating chemical interactions to tribological properties at the interface will be discussed. This work was supported by Sandia National Laboratories a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

11:20am **SS2-ThM10 Nanotribological Effects of Substrate Surface Order and Partial Fluorination for Alkanephosphonic Acid Self-Assembled Monolayers on Alumina***, **M.J. Brukman**,* University of Wisconsin-Madison*; T.D. Dunbar,* 3M Company*; R.W. Carpick,* University of Wisconsin-Madison

SAMs are of considerable interest for applications such as lubrication, corrosion protection, and water repellency, particularly at the nano-scale. Here, we compare the wettability and nano-scale friction and adhesion of two phosphonic acid self-assembled monolayers (SAMs): CF@sub 3@(CF@sub 2@)@sub 7@(CH@sub 2@)@sub 11@-PO@sub 3@H@sub 2@ (F8H11 PA) and CH@sub 3@(CH@sub 2@)@sub 17@-PO@sub 3@H@sub 2@ (H18 PA) deposited on a series of three Al@sub 2@O@sub 3@ surfaces: C- and R- plane single crystal sapphire, and an amorphous alumina layer on Si. Contact angle measurements were performed to compare the wetting of fluorinated and hydrogenated SAMs by water and hexadecane. Atomic force microscopy was then used to characterize the nano-scale dependences of adhesion and friction on SAM composition and substrate surface order. We observe differences that depend on the substrate, indicating that substrate-imposed variations in packing density and ordering have measurable nanotribological effects.

11:40am **SS2-ThM11 Tribological Behavior of Self-Assembled Double Layer Measured by a Pin-on-plate Method***, **M. Nakano**, T. Ishida, T. Numata, Y. Ando, S. Sasaki,* National Institute of Advanced Industrial Science and Technology, Japan

We investigated the tribological behavior of self-assembled double layers using pin-on-plate method in this study. Previously we have been investigated the tribological behavior of alkanethiol self-assembled monolayers using pin-on-plate method and X-ray photoelectron spectroscopy [1]. We found that the friction coefficient was dependent on the alkylchain length and that even a monolayer film has sufficient durability against friction, although the friction coefficients measured at 0.2-0.3 were slightly high. It was pointed out that formation of a new overlayer on monolayer could lead to decrease the friction. From this point of view, here we investigated the tribological behavior of self-assembled double layers using pin-on-plate method. Double layer preparation on Au substrates was performed in a glass beaker at room temperature. Substrates were first exposed to a 1 mM of mercaptohexadecanoic acid solution in ethanol for 24 h. Then, the samples were exposed to a 1 mM of copper acetate solution in ethanol for approximately 5 min. Finally, the samples were exposed to a 1 mM of octadecanethiol solution in ethanol for 24 h [2]. The frictional properties of the SAMs were examined by a pin-on-plate tribometer with a load of 30 mN and sliding speeds of 1 mm/sec (0.2 Hz). The friction coefficient on double layer was kept at 0.10-0.15 for about 30 min, indicating that the topmost octadecanethiol layer was expected to act as the mobile layer and effective to decrease the friction. Ref. [1] M. Nakano, T. Ishida, T. Numata, Y. Ando, S. Sasaki: Jpn. J. Appl. Phys. 42 (2003) 4735. [2] H. Ohno, L. A. Nagahara, W. Mizutani, J. Takagi, H. Tokumoto: Jpn. J. Appl. Phys. 38 (1999) 180.

Surface Science
Room 213B - Session SS3-ThM

Halogen and Oxygen Surface Reactions and Etching

Moderator: J.J. Boland, Trinity College Dublin, Ireland

8:20am **SS3-ThM1 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl2/Al(111)***, **A.C. Kummel**, T.J. Grassman, G.C. Poon,* University of California, San Diego **INVITED**

Non-resonant multiphoton ionization and time-of-flight mass spectrometry have been used to monitor the desorption of aluminum chloride (AlxCly) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (< 5% monolayer) monoenergetic Cl2 (0.11 eV to 0.65 eV) dosing. The desorption products in this low-coverage range show predominantly hyperthermal exit velocities under all dosing conditions. For example, with 0.27 eV incident Cl2, the etch product was found to have a most-probable velocity of 517 Â± 22 m/s at an Al(111) surface temperature of 100 K. This corresponds to 22 times the expected thermal desorption translational energy for AlCl3. Sticking probability measurements and AlxCly etch rate measurements show etching even at Cl2 coverages of less than 5% monolayer at surface temperatures between 100 K and 500 K. These experimental results are consistent with a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

9:00am **SS3-ThM3 Real-time and In-situ Surface Stress and STM Measurements and their Application to Halogen Etching of Silicon Surfaces***, **T. Narushima**, N. Kinahan, J.J. Boland,* Trinity College Dublin, Ireland

All reactions between surfaces and other species induce strain at the interface to compensate for size differences, electronegativity differences, morphology changes etc. These days, to understand detailed reaction mechanism, contribution of the strain is an important factor which cannot be ignored. The resolution of SPM, however, is poor for this purpose because it does not have absolute but relative resolution. This makes strain determination via this visual method unreliable. In this presentation, we will demonstrate how this induced strain can be determined more accurately through simultaneous surface stress measurements and STM observations as a function of time. To realise this, we have designed a special monitoring system. Surface stress can be readily measured via a capacitance method. The bending of a simple cantilever was measured as a change of capacitance between sample itself and reference electrode. Change from an initial capacitance value corresponds to sample bending which indicates the surface stress change. For surface structure observation, we used conventional STM. In this configuration, conventional direct current heating of the cantilever Si sample is not possible. To heat and prepare samples we used an infrared heating source. This method allowed us to heat sample via a non-contact and static means, which is preferable for STM observation as it induces no noise effects during imaging. At high temperature, surface stress measurements become quite difficult, because high temperature induces thermal stress at interface between heterogeneous materials of sample holder. To avoid this affect, we chose a good combination of quartz and super invar that both have low thermal expansion coefficients and almost equivalent values. We will describe the application of this system to the study of halogen etching of Si surfaces.

9:20am **SS3-ThM4 Chemically Assisted Ion Beam Etching of GaAs by Argon and Chlorine Gases: Experimental and Simulation Investigations***, **A. Rhallabi**,* University of Nantes, France*; M. Gaillard,* Veeco, France*; L. Elmonser,* IMN-LPCM, France*; G. Marcos,* LPCM-IMN, France*; A. Talneau,* LPN-CNRS, France*; F. Pommereau,* OPTO+, France*; P. Pagnod,* University of Nantes, France*; J.P. Landesman,* LPCM-IMN, France*; N. Bouadma,* France Telecom

It is now evident that the improvement of the optical and electrical performances of the III-V components depends on the optimization of the critical process steps such as the dry etch processes especially for the submicron and nanometer devices. The Chemically Assisted Ion Beam Etching (CAIBE) is one of dry etch processes where etching rate and etched surface profile are controlled by the synergy between the reactive neutral species and ion bombardment. This technique uses inert ion bombardment in a reactive gas environment to achieve a separate control between sputtering and chemical etching components. A direct injection of a reactive gas close to the surface avoids the development of chemical reactions in gas phase and allows to have a better control of the transfer of the slopes in the case of mesa structure etching and the anisotropy in the case of trench etching. Experimental investigations of the chlorine and argon CAIBE process for the fabrication of vertical, ultrahigh quality facets in GaAs are reported. The effects of CAIBE process parameters as ion current and energy, chlorine flow rate and substrate temperature on the etching rate and etched GaAs topography evolution have been analyzed. To complete the experimental study, two types of 2D CAIBE model have been developed to predict the etching rate evolution and the etching GaAs profiles through the mask. The first one is an analytical model based on the concept of adsorbed surface fraction by chlorine and the second is based on the Monte-Carlo technique to study the etched surface kinetic. For both models, the simulation and the experiment results agree well with the experiment. Finally, in order to assess the compliance of Cl2/Ar+ CAIBE etching with device applications, 980 nm Ridge lasers have been processed and their electro-optic characteristics have been compared to regular wet-chemical etched ridge stripe.

9:40am **SS3-ThM5 Semiconductor Surface Chemical Functionalization for Microelectronics Applications: Gas Phase Chlorination of H-Passivated Silicon Surfaces***, **S. Rivillon**, F. Amy, Y.J. Chabal,* Rutgers University*; M.M. Frank,* IBM

Controlling the surface chemistry of semiconductor surfaces is critical and particularly important for the growth of alternative dielectrics (i.e. other than SiO@sub 2@) on silicon surfaces. For high-k dielectrics growth using atomic layer deposition, for instance, the chemical nature of the surface determines the abruptness of the resulting interface. Chlorination of H-terminated surfaces is a powerful way to grow high-k dielectrics with minimum interfacial SiO@sub 2@ and needs to be studied. We used several different processes to chlorinate the surfaces: chlorine Cl@sub 2@ gas phase, wet chemistry and photochlorination, and investigated the resulting surfaces by infrared absorption spectroscopy looking directly at the Si-Cl modes. The surface termination is independent of the chlorination method: 1) H-terminated Si(111) surfaces are fully covered by chlorine and remain atomically flat meaning that chlorination processes do not change the surface morphology; 2) only partial chlorination of the Si(100) surface is achieved, with a high degree of disorder. The stability of both chlorinated surface has been studied under nitrogen (N@sub 2@) and in ambient atmosphere.

10:00am **SS3-ThM6 Charge-Carrier-Stimulated Halogen Desorption from Si(100)-(2x1)***, **B.R. Trenhaile**, G.J. Xu, A. Agrawal, A.W. Signor, K.S. Nakayama, J.H. Weaver,* University of Illinois at Urbana-Champaign

Scanning tunneling microscopy was used to investigate spontaneous Br atom desorption from Br-terminated Si(100)-(2x1) as a function of temperature for 620 â?" 775 K. Significantly, analysis demonstrates that the activation energy and pre-exponential factor for the desorption depend on both the doping type and concentration. Moreover, the kinetic parameters are observed to follow the compensation (Meyer-Neldel) rule, and analysis yields a characteristic energy in good agreement with the phonon Debye energy for silicon. The activation energies correspond to the antibonding Si-Br levels, and we propose that thermally-excited charge carriers produce intermediate electronic states that lead to a novel form of electron-stimulated desorption. The desorption of other halogens from Si(100) will also be discussed.

10:20am **SS3-ThM7 Morphological Evolution during Competitive Etching and Oxidation of Vicinal Si(100) Surfaces***, **M.A. Albao**, D.-J. Liu, J.W. Evans,* Iowa State University

Exposure of a vicinal Si(100) surface to oxygen at ~600C produces etching-mediated step recession. This process is impacted by the formation oxide islands which act as pinning centers for the receding steps, as observed in STM studies by Pelz et al. We develop an atomistic model for this process which accounts for the interplay between oxygen surface chemistry (adsorption, diffusion, oxide formation, and etching via SiO desorption) and the Si surface and step dynamics (anisotropic diffusion and aggregation of vacancies formed by etching with each other or with steps, and attachment-detachment dynamics at steps incorporating anisotropic energetics). Kinetic Monte Carlo simulation of this model produces etch morphologies where receding steps retain qualitative features of their equilibrium morphology (alternating rough SB steps and smooth SA steps), although pinning greatly distorts equilibrium structure (as seen in STM studies). Even without pinning, step evolution is a driven far-from-equilibrium process (as is step flow during MBE) which is impacted by the details of the etching process (e.g., anisotropic vacancy diffusion can lead to an alternation between etch pit nucleation and step flow on adjacent terraces). Simulations used to characterize the dependence of the complex etch morphologies for this model on temperature and oxygen pressure.

10:40am **SS3-ThM8 Atomic Oxygen Etching of Phosphorous-containing Polymer Surfaces***, **H. Fairbrother**, G. Wolfe, J. Torres,* Johns Hopkins University

The aerospace industry has recently developed phosphorous-containing polymers that can resist the severely oxidizing environment encountered by vehicles traveling in Low Earth Orbit (LEO). Post-flight analysis shows that upon exposure to atomic oxygen (AO) present in LEO, these polymers form a self-passivating phopshate like (P@sub x@O@sub y@)overlayer that hinders etching of the underlying bulk. The protective capabilities of these phosphorous-containing polymers, whose synthesis is complex and expensive, derive solely from the chemical characteristics of the near surface region rather than the bulk. In an attempt to develop a more cost-effective and generally applicable method of creating polymer surfaces with the ability to resist etching by AO, we have initiated studies on polyethylene (PE) ion-implanted with trimethylphosphine. X-ray photoelectron spectroscopy reveals that under ambient conditions the P-implanted PE readily oxidizes to form phosphate-containing bonds at the surface. The thickness of the phosphate layer increases with a logarithmic dependence on air exposure, indicating that the growing phosphate structure limits diffusion of oxygen species through the near-surface region. Subsequent exposure of these films to AO leads to carbon etching from the surface, leaving behind a phosphorous-rich overlayer. Related studies of thin films used to simulate the P-implanted PE surface show that these phosphate structures remain thermally stable under vacuum conditions up until ~650 K. Results from atomic force microscopy studies will also be presented to illustrate the morphological changes in the polymer surface that accompany air oxidation and AO exposure.

11:00am **SS3-ThM9 Structural Damage of Self-Assembled Monolayers Induced by 5-eV O@super +@ Bombardment***, **T.D. Tzvetkov**, X. Qin, D.C. Jacobs,* University of Notre Dame

Self-Assembled Monolayers (SAM) of decanethiol/Au(111) are bombarded with 5-eV O@super +@ ions in UHV. XPS reveals that the carbon content of the SAM decreases, while the oxygen content increases with O@super +@ dose. STM images of ion-exposed and unexposed regions of the SAM are compared. The SAM layer exhibits greater disorder after only modest doses of 5-eV O@super +@ ions. Initially, ion-induced damage occurs predominantly near domain boundaries, surface steps, and vacancies. In contrast, large defect-free surface domains show considerable stability against 5-eV O@super +@ bombardment. A mechanism for degradation of the SAM by low-energy O@super +@ ions is proposed.

11:20am **SS3-ThM10 In-situ STM-studies of Solid/Liquid Interfaces:Growth of Ultrathin Compound Films***, A. Spaenig, S. Huemann, J. Hommrich, P. Broekmann, **K. Wandelt**,* University of Bonn, Germany

Electrochemical Atomic Layer Epitaxy (ECALE) is quite an interesting alternative route for the synthesis of ultrathin layers, instead of vacuum based chemical vapour deposition techniques. This technique is based on alternating reductive and oxidative underpotential deposition (UPD) processes, e.g. of metal cations and halide or chalcogenide anions. In this contribution the growth of ultrathin semiconducting cadmium sulfide and insulating cadmium chloride films on Cu(111) and Cu(100) single crystal electrodes has been studied in-situ using an ElectroChemical Scanning Tunnelling Microscope (ECSTM). Atomically resolved ECSTM images are presented and discussed for the binary systems of either sulfide or chloride on Cu(111) and Cu(100) as well as for the ternary systems of cadmium sulfide and cadmium chloride on both surfaces. Chloride forms a (@sr@3 x @sr@3)R30° and c(2x2) adsorbate structures on Cu(111) and Cu(100), respectively, and has only a restructuring influence on the morphology of surface steps. In turn, sulfide forms several structures of low and high commensurability on both Cu surfaces, namely a c(2x6) on Cu(100) and a (@sr@7 x @sr@7)R19.1° and (2@sr@7 x 2@sr@7)R19.1° on Cu(111). Moreover at very positive electrode potentials sulfide induces severe reconstructions of both Cu surfaces with a checker-board like superstructure on Cu(100) and a hexagonal Moire like superstructure on Cu(111). Post-deposition of cadmium onto the chloride or sulfide pre-covered Cu surfaces leads to the formation of cadmium chloride or cadmium sulfide compound layers with interest periodic nanoscale superstructures whose physical properties are further characterized by ex-situ electron and ion spectroscopies.

Surface Science
Room 210C - Session SS+EM+SC-ThA

Compound Semiconductor Growth and Surface Structure

Moderator: A.R. Smith, Ohio University

2:00pm **SS+EM+SC-ThA1 III/V Semiconductor Surfaces during Metalorganic Vapor-phase Epitaxy***, **R.F. Hicks,*** University of California, Los Angeles **INVITED**

{Thin films made from compound semiconductors, such as indium phosphide, gallium arsenide and their alloys, have key applications in electronic and photonic devices. These single-crystal materials are fabricated by metalorganic vapor-phase epitaxy (MOVPE). In our laboratory, an ultra-high vacuum system has been connected to a state-of-the-art MOVPE reactor so that the semiconductor surfaces may be characterized in the growth environment. The atomic composition and structure of these materials has been determined by scanning tunneling microscopy, infrared spectroscopy, reflectance difference spectroscopy, x-ray photoelectron spectroscopy, and ab initio molecular cluster calculations. It has been found that indium phosphide and gallium arsenide exhibit very different surface structures under MOVPE process conditions. A disordered double-layer of As atoms with a few alkyl radicals are adsorbed on GaAs (001), while on InP (001), the surface is terminated with H atoms adsorbed on P dimers. This latter structure exhibits a single-domain (2x1) reconstruction. Another interesting example of III/V semiconductor surface chemistry is the formation of InGaAs/InP interfaces. Localized strain produces atomic arrangements that are distinct combinations of InP and InAs reconstructions. The application of this knowledge to the growth of epitaxial device structures will be discussed. @FootnoteText@ invited by David Castner.}

2:40pm **SS+EM+SC-ThA3 Quantitative Analysis of Indium Concentration in InGaAs Quantum Dots and Wetting Layers Using Cross-sectional Scanning Tunneling Microscopy***, N. Liu, S. Govindaraju, A.L. Holmes Jr., **C.-K. Shih,*** University of Texas at Austin

Scanning tunneling microscopy has been employed to explore self-assembled InGaAs quantum dots (QDs) grown by migration enhanced epitaxy (MEE). With atomic resolution, compositional analysis has been done for both the QDs and wetting layers quantitatively. We found that both vertical and lateral segregation play important roles during the formation of the islands and thereafter capping procedure. Depletion of the wetting layer, due to the formation of the QDs, is demonstrated. More importantly, it is found that after capping the amount of existing indium in the QDs and WL is less than that of deposited indium, indicating a portion of deposited indium atoms was evaporated to the vacuum during overgrowth of GaAs. This observation is different from previous results, which proposed indium re-distribution within GaAs matrix after capping growth. Based on the observed data, a growth model is also proposed.

3:00pm **SS+EM+SC-ThA4 Surface Science of Gallium Nitride and Related Alloys***, **R.M. Feenstra,*** Carnegie Mellon University **INVITED**

The formation and structure of various faces of GaN, including adsorbed layers of Al, In, or H, are discussed. The primary preparation method is plasma-assisted molecular beam epitaxy although a comparison of results from metal-organic vapor phase epitaxy will also be presented. Experimental results from scanning tunneling microscopy allow us to broadly determine the characteristics of the surface structures, and first principles theory is then used to determine the precise atomic arrangements. For the case of surfaces grown by vapor phase epitaxy spectroscopic ellipsometry is used to identify the relevant surface phases. In contrast to other semiconductor surfaces, a central feature of many GaN reconstructions is their tendency to form metallic overlayers of metal (Ga, In, or Al) atoms. The terminating layers of metal atoms also leads to novel aspects of the surface kinetics - N atoms are predicted to diffuse easily between the metal layers, thus yielding enhanced surface diffusivity for those surfaces which are terminated by more than one layer of metal atoms. @FootnoteText@ Work performed with Y. Dong, C. D. Lee, H. Chen, A. R. Smith (CMU); J. E. Northrup (PARC); J. Neugebauer (FHI, Berlin); C. Cobet, T. Schmidtling, M. Drago, N. Wollschlaeger, N. Esser, W. Richter (TU, Berlin); and supported by NSF and ONR.

3:40pm **SS+EM+SC-ThA6 First Scanning Tunneling Microscopy and Spectroscopy Study of c-GaN(001)-4x1 Tetramer Structure and SIESTA Surface Simulation***, **H.A. Al-Brithen,** M.B. Haider, N. Sandler, A.R. Smith,* Ohio University*; P. Ordejon,* Institudo de Cienias de Materiales, Spain

Although early papers of the surface structure of c-GaN(001) reported 2x2 and c(2x2) reconstructions,[a] it was later shown both experimentally[b] and theoretically[c] that the intrinsic reconstruction is 4x1. However, until now, this 4x1 reconstruction has never been reportedly observed in real space. We have grown c-GaN on MgO(001) using radio frequency nitrogen plasma molecular beam epitaxy under Ga-rich conditions. RHEED patterns show that GaN(001) clearly exhibits 1x1 reconstruction during and after the growth; in fact, after cooling to ~ 200 °C a reversible disorder-order transition from 1x1 to 2x occurs, which may have been neglected or confused in earlier experiments with 2x2. This 2x is imaged using STM, finding that it is actually c(4x16) for Ga-rich growth and c(4x20) for more Ga-rich growth; STS spectra suggest that GaN(001)-c(4x16) is metallic. Annealing the film at T@sub s@ ~ 700-800 °C leads to the 4x1 reconstruction, as indicated by RHEED. STM performed on c-GaN(001)-4x1 shows that the surface consists of rows aligned along [110] with row spacing of 12.8 Å. Dual-bias STM images show a 180@super o@ phase shift of the filled and empty states profiles, as the sample bias changes from -1.2 V to +1.2 V, consistent with our recent simulated STM images, calculated using SIESTA code based on the tetramer model, showing that the filled state peak centered on the tetramer corresponds to the empty state minimum. STS acquired on the tetramer surface agrees with the semiconducting nature of 4x1, having a surface gap of 1.3 eV. In fact, the 4x1 tetramer structure was also predicted for c-AlN(001)[d], which widens the importance of understanding this reconstruction. Work is supported by NSF. @FootnoteText@ [a] Brandt et al., Phys. Rev. B R2253 (1995). [b] Feuillet et al., Appl. Phys. Lett. 70(8) (1997). [c] Neugebauer et al., Phys. Rev. Lett. 80(14) (1998). [d] Felice et al., Appl. Phys. Lett. 74(15) (1999).

4:00pm **SS+EM+SC-ThA7 Ion Induced Step Debunching of GaN***, **B. Cui,** P.I. Cohen,* University of Minnesota*; A.M. Dabira,* SVT Associates, Inc.

The development of surface morphology during ion bombardment has been described in terms of the curvature dependence of the sputtering yield [1] and asymmetric kinetics for the attachment of surface adatoms and vacancies at step edges [2]. We have used a Kaufman ion source to study the low energy ion effects during the MBE growth of GaN on sapphire substrates and GaN templates, comparing the results to these models. From a macroscopic point of view our measurements on GaN show quantitative agreement with the curvature driven theories. In particular we use the cross-over between Ga-limited growth and N-limited growth to estimate the N adatom concentration, a key ingredient of the theory. From a microscopic view, however, our RHEED and AFM studies have observed step debunching of multilayer steps and the elimination of hillock spirals. In these measurements, the starting GaN(0001) templates had 20 layer high mesas. After growth, round, nanoscale dimple structures, ranging from 90 nm to 850 nm, with bilayer steps were produced. This was seen with both Ar and nitrogen ions at energies ranging from 100-1200 eV. The size of the dimples and the terrace length of the debunched steps decrease with increasing sample temperature. After ion assisted growth, islands are found at the edges of the debunched steps. By tuning the ion energy and growth rate, uniform distributions of GaN nanoparticles, with means ranging from 50 nm to 200 nm, can be prepared. By combining ion induced step debunching and growth, step flow growth at the debunched steps is obtainable. Partially supported by the NSF and the AFOSR. @FootnoteText@ 1. R. M. Bradley and J. M. E. Harper, J. Vac. Sci. Technol. A 6, 2390 (1988). 2. J. Kim, D. G. Cahill, and R. S. Averback, Phys. Rev. B 67, 045404 (2003).

4:20pm **SS+EM+SC-ThA8 Thermal Desorption of Deuterium from GaN(0001): A Sensitive Probe of Surface Preparation***, **C.M. Byrd,** J.N. Russell, Jr.,* Naval Research Laboratory

Gallium nitride (GaN) is a wide band gap semiconductor with applications in high temperature, power and frequency optoelectronic devices. The surface chemistry of hydrogen on GaN affects growth rates and electronic passivation, while annealing temperatures impact both ohmic contacts and thermal stability. In this work, the preparation of a GaN(0001) thin film surface was investigated as a function of anneal temperature (300-1100K) using Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED), and temperature programmed desorption (TPD). After the GaN(0001) surface was sputter cleaned with nitrogen (N@sub 2@@super +@) ions, N@sub 2@ desorption was observed at 950 K from embedded nitrogen and then above 1200 K from GaN decomposition. EELS and AES showed subtle changes as the anneal temperature increased, and the LEED pattern sharpened. TPD spectra were collected for a series of anneal temperatures. After annealing the surface and cooling to room temperature, the surface was dosed with D atoms. When heated at 1 K/s, D@sub 2@ thermal desorption was observed, but not ammonia or gallane. There were four D@sub 2@ thermal desorption peaks at 430, 600, 730 and 810 K, the appearance and relative intensities of which were related to whether the anneal occurred at, above, or below the embedded nitrogen desorption temperature. Correlation of the anneal temperature dependence of the D@sub 2@ thermal desorption with the EELS, AES, and LEED data aided in identifying the origins of the D@sub 2@ desorption states. This work demonstrates D@sub 2@ thermal desorption is very sensitive to the quality of the GaN(0001), and explains differences in hydrogen on GaN(0001) TPD results in the literature.

4:40pm **SS+EM+SC-ThA9 Metal/Semiconductor Phase Transition in CrN Grown by Molecular Beam Epitaxy and Scanning Tunneling Microscopy***, **C. Constantin**, M.B. Haider, A.R. Smith,* Ohio University

Considerable interest has been of late in transition metal nitrides thin films/surfaces, which have both magnetic and electronic properties with potential applications in spintronics. CrN is a particularly interesting case, having a known correlation of structural and magnetic transition from a B@sub 1@ NaCl-paramagnetic to an orthorhombic-antiferromagnetic at T@sub Neel@=273-286K@footnote 1@. However,the reported electronic properties of CrN are controversial, and there has been no consensus whether the material is a metal or a semiconductor@footnote 2,3@. In this study, CrN is grown on MgO(001) at a substrate temperature of 450°C by a novel molecular beam epitaxy method for obtaining smooth surfaces. Bulk measurements reveal that the films are single crystal, and stoichiometric. The 1x1 face-centered cubic (fcc) surface structure is clearly distinguishable as obtained (for the first time) in room temperature atomic resolution scanning tunneling microscopy. In addition to the atomic resolution, long-range topographic distortions [LTD] are also seen on the surface, as also observed for the semiconductor ScN (001)@footnote 3@ and other nonpolar III-V surfaces. LTDs are characteristic of semiconductor surfaces, and are related to localized charge accumulation from impurities. Resistivity was measured from 77 to 450K; metallic behavior is found up to 260K (in contrast with some earlier reports) and semiconductor behavior above 285K. The bandgap obtained from resistivity data,71±0.315meV, agrees with the tunneling spectroscopy of the surface which show a very small gap. Consistent results have now emerged in which CrN has a semiconductor-metal phase transition corresponding to its magnetic transition. @FootnoteText@ @footnote 1@ A. Filippetti et.al, Phys. Rev. B 59, 7043 (1999)@footnote 2@J. D. Browne et.al, Phys. Status Solidi 1, 715 (1970)@footnote 3@P. S. Herle et.al, J. Solid State Chem. 134, 120 (1997)@footnote 4@H. A. Al-Brithen et.al, submitted to Phys. Rev. B.

Surface Science
Room 210B - Session SS1-ThA
Metal Oxides and Clusters IV: Oxide Surface Chemistry

Moderator: F. Zaera, University of California Riverside

2:00pm **SS1-ThA1 Partial Dissociation of Water on the Surface of ZnO***, **B. Meyer**, D. Marx,* Ruhr-Universität Bochum, Germany*; O. Dulub, U. Diebold,* Tulane University*; M. Kunat, D. Langenberg, C. Wöll,* Ruhr-Universität Bochum, Germany

Due to the interplay between chemical bonding, van der Waals forces, and hydrogen bonding, the interaction of water with solid substrates gives rise to complex phenomena such as complete dissociation, partial dissociation at defects, multilayer formation, and wetting. Recently, an intriguing, yet controversial, intermediate scenario was advanced, where the interaction between water molecules results in a partial dissociation of water on perfect surfaces, leading to superlattices with long-range order. Applying a broad array of methods, including diffraction (He-atom scattering, LEED), scanning tunneling microscopy, and thermodynamic measurements supplemented by density-functional total-energy, Car-Parrinello molecular dynamics, and STM computations, conclusive evidence is given that such a phenomenon is encountered for H@sub 2@O on the perfect ZnO(10-10) surface. At monolayer coverage, every second water molecule is found to auto-dissociate, subject to a low activation barrier, upon a favorable hydrogen-bonding interaction with a neighboring water molecule, i.e. without the need to invoke defects or impurities. This process leads to a (2x1) superlattice with long-range order which is stable from well below room temperature up to temperatures close to the boiling point of liquid water.

2:20pm **SS1-ThA2 Photoemission of Adsorbed Xenon Studies on the Characterization of Reaction Sites on Oxygen-Modified Ni(110) Surfaces***, **H. Guo**, F. Zaera,* University of California at Riverside

Considerable attention has been paid in our laboratory to the study of the adsorption and reactions of surface intermediates of relevance to catalysis on clean, hydrogen- and oxygen-modified Ni(110) to understand the properties of these surfaces in hydrocarbon conversion, and in trying to identify specific sites selective for the promotion of desirable reactions. STM studies have evidenced that surface oxygen in lower coverage regimes not only induces reconstruction of Ni(110) in extending domains, but also modifies the electronic structure at local sites. Such surfaces have been found particularly effective in the production of heavier hydrocarbons. However, the relationship between this distinctive catalysis and the surface structures responsible for it cannot be established without a better knowledge of the local surface properties at the atomic scale. With this in mind, we have carried out experiments using photoemission of adsorbed xenon (PAX) to characterize specific adsorption sites in heterogeneous surfaces produced by oxygen adsorption on Ni(110) single crystals. This technique, which provides both energetic and local electronic information on small surface atom ensembles, has been used in combination with chemical titrations using probe molecules such as carbon monoxide and ammonia to determine correlations between electronic structures and reactivity. It was determined that ammonia prefers a direct interaction with the terminating atoms of the -Ni-O- added rows that form on Ni(110) upon oxygen treatments. Those sites appear to be key for the selective conversion of hydrocarbons.

2:40pm **SS1-ThA3 Oxide and Carbonate Surfaces as Environmental Interfaces: The Importance of Water in Surface Composition and Surface Reactivity***, **V.H. Grassian**,* University of Iowa **INVITED**

Environmental molecular surface science is an important and expanding area of current research. This presentation focuses on advances in the molecular level understanding of the chemistry that occurs on oxide and carbonate surfaces in the atmosphere. In particular, the importance of water in the surface composition and surface reactivity of two representative oxide and carbonate surfaces, MgO(100) and CaCO@sub3@(104) will be discussed. Reactions of trace atmospheric gases, including HNO@sub3@, with MgO(100) and CaCO@sub3@(104) as a function of relative humidity highlight the role of surface hydroxyl groups and molecularly adsorbed water in these reactions.

3:20pm **SS1-ThA5 Interactions of S-containing Molecules and Water Vapor with Polycrystalline UO@sub 2@***, **B.V. Yakshinskiy**, T.W. Schlereth, M.N. Hedhili, T.E. Madey,* Rutgers, The State University of New Jersey

The interaction of sulfur dioxide (SO@sub 2@), thiophene (C@sub 4@H@sub 4@S) and water vapor (D@sub 2@O) with a polycrystalline stoichiometric UO@sub 2@ and oxygen-deficient UO@sub 2@ surfaces has been studied under UHV conditions over the temperature range 100 K to 600 K, using XPS (X-ray photoelectron spectroscopy) and TPD (temperature programmed desorption). This work is motivated by potential catalytic applications of stockpiles of depleted uranium. All three molecules are relatively unreactive on the stoichiometric UO@sub 2@ surface, they adsorb and desorb in molecular form. The creation of oxygen vacancies by 1.5 keV Ar ion sputtering is found to enhance the UO@sub 2@ surface reactivity towards the desulfurization of C@sub 4@H@sub 4@S and SO@sub 2@ and the dissociation of water with formation of OD species. Heating of the oxygen-deficient surface with a preadsorbed water monolayer causes desorption of molecular D@sub 2@. The oxygen remains and restores the sample surface to its initial stoichiometric state. The healing of sub-surface defects occurs through thermal diffusion of atoms from the sample bulk at ~ 500 K.

3:40pm **SS1-ThA6 Reactions of Substituted Hydrocarbons with Cerium Oxide Thin Films@footnote1@***, **D.R. Mullins**, M.D. Robbins, T.S. McDonald,* Oak Ridge National Laboratory

Fully oxidized ceria surfaces are largely inactive with respect to the adsorption and reaction of most adsorbates under UHV conditions. Reduced surfaces, however, provide active sites where some adsorbates such as H@sub 2@O, NO and SO@sub 2@ can adsorb and react. Other molecules, such as CO, H@sub 2@ and C@sub 2@H@sub 4@ do not interact strongly with either an oxidized or a reduced surface. Based on the ethylene behavior, it appears that hydrocarbons may not interact strongly with ceria whereas on metals they frequently decompose. Substituted hydrocarbons may therefore bind to the surface through the heteroatom at the oxygen vacancy while the hydrocarbon part of the molecule may not interact strongly with the surface. We have recently completed a study of methanol and methanethiol adsorption on ceria as a function of temperature, exposure and Ce oxidation state. CH@sub 3@OH reacts at low temperatures with oxidized CeO@sub 2@ to produce H@sub 2@O at 200 K, and CH@sub 2@O and CH@sub 3@OH near 600 K. This leads to the reduction of the ceria. This is the first molecule we have examined that is capable of reducing a ceria film in UHV. Surprisingly, CH@sub 3@SH does not interact strongly with the CeO@sub 2@. It desorbs molecularly by 300 K and does not reduce the oxidized surface. On reduced ceria, the oxygen vacancies result in more methanol adsorption which undergoes more extensive decomposition producing CO and H@sub 2@ near 600 K. As the degree of ceria reduction increases, more H@sub 2@ and less H@sub 2@O are produced. Methanethiol does adsorb on the reduced surface producing CH@sub 3@S and OH. The C-S bond cleaves near 600 K and methyl reacts with the hydroxyls to produce CH@sub 4@. @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.

4:00pm **SS1-ThA7 Adsorption and Reaction of Acetaldehyde and Methanol on Stoichiometric and Defective Mixed-Metal Oxide Surfaces***,* ***L.Q. Wang****, S.A. Azad, K.F. Ferris, C.H.F. Peden, M.H. Engelhard,* Pacific Northwest National Laboratory

The adsorption and reaction of oxygenated hydrocarbons on metal oxide surfaces are of much interest from both fundamental and practical perspectives. The reactivity of these catalytic processes largely depends on the characteristics of the oxide catalysts defined by their surface structures, acid-base properties and surface defects. Oxygenated hydrocarbons are often used as fuels and fuel additives , and they may be formed as a result of incomplete combustion of fuel in the engine. To efficiently reduce these toxic exhaust products, it is especially helpful to have a fundamental understanding of the adsorption and reaction of oxygenated hydrocarbons on metal oxide surfaces. In this presentation, we examined the interactions of acetaldehyde and methanol with stoichiometric and defective SrTiO@sub 3@(100) surfaces using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and first-principles density-functional calculations. The results obtained from methanol and acetaldehyde on SrTiO@sub 3@(100) surfaces are compared with our results on Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces and with the previous results on single crystal TiO@sub 2@ surfaces. Both acetaldehyde and methanol adsorb mostly non-dissociatively on the stoichiometric SrTiO@sub 3@(100) surface that contains predominately Ti@super 4+@ cations. Theoretical calculations predict weak adsorption of acetaldehyde and methanol on TiO@sub 2@-terminated SrTiO@sub 3@(100) surfaces, in agreement with the experimental results. The stronger binding of acetaldehyde and methanol on TiO@sub 2@ surfaces than on SrTiO@sub 3@(100) surfaces is attributed to the more covalent nature of the Ti@super 4@@super +@ cation sites in the mixed-metal oxides and the unique surface structure due to the absence of the bridging oxygen atoms on the TiO@sub 2@-terminated SrTiO@sub 3@(100). The Ti@super 4@@super +@ sites on the stoichiometric SrTiO@sub 3@(100) surface are not sufficiently active for surface reactions such as aldol condensation, as opposed to the Ti@super 4@@super +@ ions on the TiO@sub 2@ (001) surface. However, decomposition and redox reactions for both methanol and acetaldehyde occur in the presence of surface defects created by Ar@super +@ sputtering. The decomposition products following reactions of acetaldehyde on the defective surface include H@sub 2@, C@sub 2@H@sub 4@, CO, C@sub 4@H@sub 6@ and C@sub 4@H@sub 8@. Reductive coupling to produce C@sub 2@H@sub 4@ and C@sub 4@H@sub 8@ is the main reaction pathway for decomposition of acetaldehyde on the sputter reduced SrTiO@sub 3@(100) surface. Adsorption of CH@sub 3@OH on the reduced SrTiO@sub 3@(100) surface produces the decomposition products of H@sub 2@, CO, and CH@sub 4@. As compared with SrTiO@sub 3@(100) surfaces, Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces exhibit enhanced adsorption and reactivity for methanol and acetaldehyde. Both acetaldehyde and methanol mostly adsorb dissociatively on the oxidized Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces. The formation of furan was surprisingly observed on reduced Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) surfaces following the adsorption of acetaldehyde.

4:20pm **SS1-ThA8 The Adsorption of Bromobenzene on Periodically-Stepped and Flat NiO(100) Surfaces***,* ***S.C. Petitto****, E.M. Malone, M.A. Langell,* University of Nebraska-Lincoln

Bromobenzene was adsorbed onto both stepped and flat NiO(100) surfaces to model surface defects relevant to heterogeneous chemical processes. Both surfaces were characterized using Auger electron (AES) and X-ray photoelectron (XPS) spectroscopies, low energy electron diffraction (LEED), and thermal desorption mass spectrometry (TDS). The stepped NiO(100) substrate was cut and polished at an angle vicinal to the (100) surface, resulting in monoatomic steps with 7-atom terraces. The LEED diffraction patterns show sharp diffraction features for both surfaces, and diffraction spot splitting correlating to appropriate terrace and step height dimensions for the stepped surface. Both substrates interact with bromobenzene at 120 K to produce first a molecularly adsorbed monolayer species and then a multilayer adsorbate state as the exposure is increased. The stepped NiO(100) surface has an additional TDS peak not observed for flat NiO(100) and which results in dissociation adsorption initiated by cleavage of the Br-C@sub 6@H@sub5@ bond. Bromine that remained on the surface appeared as nickel bromide.

4:40pm **SS1-ThA9 Synchrotron X-Ray Photoelectron Spectroscopy Studies of the Thermal Chemistry of (trimethyl) Methylcyclopentadienyl Platinum on Tio@sub 2@ (110)***,* ***K. Adib****,* Brookhaven National Laboratory*; M.A. Barteau,* University of Delaware*; J. Hrbek,* Brookhaven National Laboratory*; J.M. White,* University of Texas at Austin

Pt/TiO@sub 2@ is one of the most important systems used in the photocatalytic decomposition of water to hydrogen as well as environmental purification of organic waste. In this regard, the use of organometallic precursors as sources of Pt metal islands on TiO@sub 2@ surfaces offers an attractive alternative to metal-vapor deposition techniques. We have used synchrotron X-ray photoelectron spectroscopy (XPS) to investigate the thermal chemistry of (trimethyl) methylcyclopentadienyl platinum (MeCpPtMe@sub 3@) on the stoichiometric rutile (110) surfaces. Our results indicate that the submonolayer adsorption of MeCpPtMe@sub 3@ on nominally stoichiometric TiO@sub 2@ (110) at 300 K does not result in substantial decomposition of the adsorbate. While subsequent annealing of the surface to 450 K enhances the decomposition of the MeCpPtMe@sub 3@, as evidenced by the appearance of additional Pt 4f peaks, there is no evidence of the desorption of the resulting carbon fragments even after extended periods of annealing. Predosing of nominally stoichiometric TiO@sub 2@ (110) surfaces with molecular oxygen at 300 K substantially enhances the decomposition of subsequently deposited MeCpPtMe@sub 3@. This decomposition is accompanied by the formation surface-bound CO@sub x@ species, possibly carboxylate groups, suggesting strong interactions between the adsorbate and substrate. Heating to 850 K can result in the removal of more than 98% of the surface bound carbon species, including the CO@sub x@, but does not result in the formation of a carbon-free Pt/TiO@sub 2@ surface.

5:00pm **SS1-ThA10 The Reaction of DL-Proline on TiO@sub2@(110) Single Crystal Surfaces.***, K. Adib,* Brookhaven National Laboratory*; G. Fleming,* University of Auckland, New Zealand*; J.A. Rodriguez,* Brookhaven National Laboratory*;* ***H. Idriss****,* University of Auckland, New Zealand*; M.A. Barteau,* University of Delaware

Titanium metal is widely used as a medical implant in the aiding of healing fractures in teeth and bone. The choice of titanium as an implant material is based on both its mechanical properties and on its relative chemical inertness. Once placed in the body's aqueous environment, the implant undergoes an oxidation process where the formation of a thin oxide layer in the range of 10 to 100 nm thick occurs. This layer is crucial since it prevents the Ti metal from further reacting with the biological molecules. However, the nature of interaction of the bio-molecule with this thin TiO@sub2@ surface will ultimately determines its conformation. If the conformation of the bio-molecule is altered from its naturally occurring state, it may cause the body to undergo an auto immune response and reject the implant. Surface science studies can address the nature of interaction of prototype amino acids with TiO@sub2@. In this work we study the reaction of DL-Proline on the surface of a model TiO@sub2@ surface, the rutile (110) surface. Proline was chosen as it is a constituent of collagen I, a major high tensile structural protein found in teeth, bone and cartilage. The reaction of DL-Proline on stoichiometric and O-defected surfaces has been investigated by temperature programmed desorption while the surface species at different reaction temperatures were monitored by X-ray core level shifts and by their valence band. Proline binds to the surface via its COO group. The presence of two N(1s) lines upon adsorption at 300 K indicates the presence of two distinct species that are tentatively assigned to -NH@sub2@@super+@- and -NH- attributed to the zwitterionic and non-zwitterionic forms of the amino acid, respectively. Complex reactions are seen for Proline upon heating the surface, and products such as CH@sub2@=C=O and HCN are seen in the gas phase. In addition, large amounts of organic species containing O and N are still present on the surface even after heating to 600 K.

Surface Science
Room 213B - Session SS3-ThA
Surface Diffusion and Transport

Moderator: L. Bartels, University of California, Riverside

2:00pm **SS3-ThA1 Molecular Transport on the Nano-Second Timescale; Co/cu(001).***, **G. Alexandrowicz**[1],* University of Cambridge, UK*; A.P. Jardine,* University of Cambridge, UK, U.K.*; H. Hedgeland,* University of Cambridge, UK*; P. Fouquet,* Institut Laue-Langevin, France*; S. Dworski, W. Allison, J. Ellis,* University of Cambridge, UK

The measurement of surface diffusion on microscopic length scales presents a considerable experimental challenge. Measurements are typically restricted to specific systems which either diffuse sufficiently slowly for real time techniques, such as STM, to be applied or fast enough to be seen using Quasielastic Helium Atom Scattering (QHAS). Here, we present the first surface diffusion measurements from the unique new Cambridge @super 3@He Spin Echo Spectrometer@footnote 1@@footnote 2@. The apparatus makes use of the @super 3@He Spin Echo technique@footnote 3@ to improve upon existing QHAS resolution by three orders of magnitude, showing new insights into previously inaccessible experimental regimes. We have studied the prototypical molecular system; CO/Cu(100). Existing QHAS measurements on this system were very limited@footnote 4@ and the intense debate over the difference between potential energy surfaces extracted from the measurements and from first principle calculations@footnote 5@ was left unresolved. Our measurements show the system is diffusing well within the previously unmeasurable regime. Quasielastic broadenings were measured as function of momentum transfer and temperature and interpreted using MD simulations. The analysis reveals a Potential Energy Surface, illustrating the success and limitations of recent first principle calculations@footnote 6@, and serves as a bench mark for further theoretical improvements. @FootnoteText@ @footnote1@ AP Jardine, P Fouquet , S Dworski, G Alexandrowicz, J Ellis, W Allison, To be published @footnote2@ S Dworski, G Alexandrowicz, P Fouquet, AP Jardine, W Allison, J Ellis. Rev. Sci. Inst. In press. 2004. @footnote3@ C Shmidt, D Scholz, U Spinola, M Dekivit, D Dubbers. Phys. Rev. Lett. 75(10):1919-1922 @footnote4@ AP Graham, JP Toennies, Surf. Sci. 427-428 (1999) @footnote5@ Q G, DA King, J. Chem. Phys. 114(2001) 1053 @footnote6@ P Fouquet, RA Olsen, EJ Baerends, J. Chem. Phys. 119(2003) 509-514.

2:20pm **SS3-ThA2 CO Diffusion on Cu(111): Effects of CO-CO Interactions***, **B.V. Rao**, R. Perry, A. Liu, L. Bartels,* University of California, Riverside

Diffusion is the surfaces process that occurs most frequently and, thus, may arguably be regarded the most important one. With the advent of low-temperature scanning tunneling microscopy one is able to image and track the motion of individual atoms and molecules on surfaces for long periods of time@footnote 1@. We probed the diffusion of CO molecules on Cu(111) at temperatures between 17 and 50 K. At 17K, molecular hops are infrequent and occur on the time-scale of hours, whereas at 50K the hopping frequency has reached >1 Hz. Measurements at various temperatures indicate that the diffusion of isolated CO molecules follows an Arrhenius behavior. Our investigation puts special attention on the effect of neighboring CO molecules on the hopping direction and frequency. Preliminary results suggest, that the CO-CO interaction enhances or decreases CO diffusion depending on the separation of the molecules. The distance dependence resembles the oscillation patter of the Cu(111) surface state, similar to Cu adatom interactions previously reported by Repp et al.@footnote 2@. @FootnoteText@ @footnote 1@Briner, B.G., Doering, M., Rust, H.-P., Bradshaw, A. M., Science 278 (1997) 257.@footnote 2@Repp J., Moresco F., Meyer G., Rieder K.H., Hyldgaard P., Persson M., Phys. Rev. Lett., 85 (2000) 2981 .

2:40pm **SS3-ThA3 How Trace Amounts of S Enhances Self-Diffusion on Cu(111)***, W.L. Ling, **K.F. McCarty**, J. De la Figuera, K. Pohl, N.C. Bartelt,* Sandia National Laboratories

We find that <0.01 monolayer (ML) of S enhances surface diffusion on Cu(111) by several orders of magnitude. Using low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM), we probe the mechanisms of this enhancement by monitoring the decay rate of island stacks and the ripening of 2D island arrays as a function of S coverage and temperature. The decay rate of islands in stacks increases roughly as the S coverage cubed, consistent with the proposal that the enhanced surface diffusion is due to the formation of Cu@sub 3@S@sub 3@ clusters@footnote 1@. However, we also find a dramatic change in the mechanism of island-stack decay and the ripening of 2D island arrays as a function of S coverage. While island decay on clean Cu is diffusion limited@footnote 2@, this is not the case in the presence of a small amount of S. However, at higher S coverages, the kinetics revert to diffusion limited. Similarly, how island arrays evolve is strongly influenced by the S coverage. For clean Cu and at high S coverages, large islands grow at the expense of nearby small islands. In contrast, local ripening does not occur with smaller amounts of S -- mass flows from islands to the steps bounding large terraces. We show that the strong dependence of the surface kinetics on S coverage can be quantitatively understood if the Cu diffusion at low S coverages is limited by the rate of reaction of S and Cu to form Cu@sub 3@S@sub 3@ clusters. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000. @FootnoteText@ @footnote 1@P.J. Feibelman, Phys. Rev. Lett. 85, p. 606 (2000).@footnote 2@M. Giesen & H. Ibach, Surf. Science 431, p. 109, (1999) .

3:00pm **SS3-ThA4 Diffusion of Ir and W Atoms on W(110) @super *@***, **G. Antczak**, G. Ehrlich,* University of Illinois at Urbana-Champaign

Using field ion microscopy we have carried out extensive measurements of the migration of Ir and W atoms on the W(110) plane at temperatures from 300 to 370 K. In addition to nearest-neighbor jumps in the direction, we recognized three types of long jumps, which may contribute to diffusion: double jumps along , vertical jumps in the direction and the horizontal jumps in the direction. From analysis of the distribution of displacements, constructed from at least 1200 observations, we have found that long jumps play a significant role in diffusion at temperature higher than 340 K. The temperature dependence of all types of jumps was measured to derive activation energies and prefactors for diffusivities. Long jumps proceed with a higher activation energy and a higher prefactor than do single jumps for tungsten as well as for iridium atoms. The rate of single jumps is diminished by contributions from long jumps. However, contrary to expectation, the presence of long jumps does not raise the prefactor for diffusivity above the usual value. Comparisons are made of Ir with W and simple models accounting for our finding are proposed. @super *@Supported by the Department of Energy under Grant No. DEFG02-96ER45439 to the Materials Research Lab., and by the Petroleum Research Fund, under Grant ACS PRF No. 36919-AC5.

3:20pm **SS3-ThA5 Temperature-Dependent Thresholds for Ion-Stimulated Surface Diffusion: A Comparison of Si and Ge Substrates***, Z. Wang, **E.G. Seebauer**,* University of Illinois at Urbana-Illinois

Ion-surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. The governing kinetic phenomena are often tacitly considered to lie at one of two poles: physical effects where momentum matching dominates, and chemical effects involving thermal activation of atomic bonds according to Arrhenius expressions. Here we report surface diffusion measurements demonstrating behavior that lies at neither pole. Optical second harmonic microscopy is used to image diffusion of indium adsorbed on Si(111) and Ge(111) under low-energy noble-gas ion bombardment. Both systems exhibit a surprising tradeoff between substrate temperature and the energy threshold at which ion influences become manifest. Molecular dynamics simulations suggest that the effect originates from changes in surface point defect concentrations. Instantaneous nonuniformities in net surface potential induced by thermal vibrations provide a mechanism by which ions can affect these concentrations nonlinearly. The effects generally increase the rate of mass transport across the surface. The simulations and experiments agree in finding that an important factor determining the magnitude of the tradeoff is the strength of the adsorbate-substrate bond, which is lower for In/Ge than for In/Si.

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

3:40pm **SS3-ThA6 LEEM Observation of Island Decay on Si(110)**, ***F. Watanabe***, *S. Kodambaka, W. Swiech, G.D. Cahill,* University of Illinois at Urbana-Champaign

Laser texturing enables the observation of island decays on (1x1) high temperature phase of Si(110) surface in low energy electron microscopy by artificially creating large flat terraces. At temperatures above the phase transition (T = 790 ~ 980 Â°C), the decay of the island areas exhibits a nonlinear dependence on time, indicating the rate limiting process is surface diffusion. The aspect ratios of the islands during the decay show a weak temperature dependence. Following a methodology developed previously@footnote 1@, we have obtained kinetic parameters involved in the island decay. The activation energy of mass transport and the free energy of kink formation have been determined to be 1.67 Â± 0.15 eV and 0.22 Â± 0.03 eV respectively. Based on this value for the kink energy and the equilibrium island shapes, we derive the angular dependence of the step energy and the step stiffness. @FootnoteText@ @footnote 1@ S. Kodambaka, V. Petrova, S. V. Khare, D. D. Johnson, I. Petrov, and J. E. Greene, Surf. Sci. 513, 468 (2002).

4:00pm **SS3-ThA7 Effects of Si Deposition on Electromigration Induced Step Bunching on Si(111)**, ***B.J. Gibbons,*** The Ohio State University*; J. Noffsinger,* The University of Kansas*; J.P. Pelz, C. Ebner,* The Ohio State University

We have studied the effects of Si deposition on direct current (DC) heating induced step bunching on Si(111) using Si samples with spherical dimples ground into the surface to create a range of surface miscut. With no Si deposition, we observe the well-known behavior that only "step-down" current produces bunching in temperature "Regime I": (<950°C), while bunching in "Regime II": (1050°C-1250°C) only occurs for "step-up" current. But in contrast to a report by Métois et al. [Surf. Sci. 440 (1999) 407] we very clearly do not observe that net growth conditions reverses the current direction required for bunching in Regime II. This is not consistent with the proposal [S. Stoyanov, Surf. Sci. 416 (1998) 200] that the primary bunching mechanism in Regime II is due to increased step permeability. However we do observe that there is a strong reduction in the density of "crossing steps" close to zero net deposition/sublimation conditions, qualitatively consistent with the simultaneous bunching/debunching model of Kandel and Weeks [Phys. Rev. Lett. 74 (1995) 3632]. We will discuss on-going work to quantify this reduction and compare it with 1D analytic and 2D Monte Carlo models. By measuring areas of the dimpled samples with different miscut, we have also found that the average step bunch height increases roughly linearly with sample miscut, but does not depend significantly on Si deposition conditions. We are also comparing this observed bunch-height dependence on miscut with 1D and 2D models to evaluate which existing model can best explain a range of step-bunching behavior. Work supported by NSF Grant DMR-0074416.

4:20pm **SS3-ThA8 Pb/Si(111) Domain Boundary Fluctuations***,* ***D.B. Dougherty***, University of Maryland at College Park*; W.G. Cullen, E.D. Williams,* MRSEC

The techniques of fluctuation statistics are applied to a common 1D interface on solid surfaces: a domain boundary between two surface phases. We describe variable temperature STM observations of fluctuating boundaries between Si(111)-(1x1)-Pb and Si(111)-@sr@3x@sr@3R30-Pb@footnote 1@. We establish the dominant mass transport mechanism for the fluctuations from the power-law growth in time of the temporal correlation function with an exponent of about 0.5. This behavior implies that fluctuations of the (1x1) boundaries occur via exchange of mass with a 2D adatom gas on the @sr@3x@sr@3 phase. This conclusion is corroborated by the extraction of the persistence probability from the same data, giving a persistence exponent of 0.75. This 2D exchange mechanism allows comparison of the nanoscale fluctuation kinetics with previous macroscopic surface science measurements. The 2D adatom gas has long been established for this system from the observation of zeroth-order desorption kinetics. Previous studies indicate a barrier for this rate-limiting exchange step of 2.3 eV@footnote 2@. Our experimental correlation functions yield an effective activation barrier of about 1.6 eV. This provides a direct physical confirmation of the indirect deduction of 2D exchange of mass at the domain boundary. Finally, the autocorrelation function of the boundary fluctuations can also be determined and used to extract correlation lengths that compare well with the size of (1x1) domains. In addition, these lengths are compared with correlation lengths for fluctuating steps on clean metal surfaces. *Supported by UMD-NSF-MRSEC under DMR-00-80008. @FootnoteText@ @footnote 1@ J. Slezak et al., Surf. Sci. 454 (2000) 584; O. Custance et al., Surf. Sci. 482 (2001) 878.@footnote 2@ M. Saitoh et al., Surf. Sci. 154 (1985) 394.

4:40pm **SS3-ThA9 Temperature-Dependence of Submonolayer Island Structure and Multilayer Growth Morphologies in Ag/Ag(111) Homoepitaxy***,* ***M. Li****, E. Cox, C. Chung, C. Ghosh, J. Evans, P.A. Thiel,* Iowa State University

We have performed STM studies to analyze the irregular structure of submonolayer islands and the rough wedding-cake-like multilayer growth morphologies formed during Ag/Ag(111) homoepitaxy between 120-180K. Previous STM and surface scattering studies have probed only selected aspects of these features of film structure, which are expected due to restricted periphery diffusion (PD) and limited interlayer transport. However, no comprehensive real-space characterization of film morphology across this temperature regime has been available. KMC simulation of atomistic lattice-gas models is also viable in this regime where island separations are below ~100nm, and film morphology is not controlled by dislocations (in contrast to behavior at 300K). We have thus also developed a realistic atomistic model to describe the submonolayer growth of individual islands, and thereby quantified the observed transition with increasing temperature from dendritic shapes with triangular envelopes (due to anisotropy in incorporation at corners) to more isotropic fractal shapes (reflecting high edge and kink rounding barriers), and then to compact shapes (reflecting efficient PD). More complete modeling of the overall island nucleation and growth process revealed a transition to reversible island nucleation in this temperature range. Finally, by extending of our realistic model for submonolayer island formation to the multilayer regime incorporating negligible interlayer transport, we described quantitatively the observed kinetic roughening and wedding-cake-like growth morphologies.

Surface Science
Room 210B - Session SS1-FrM
Hydrated Surface Phenomena

Moderator: E. Stuve, University of Washington

8:20am **SS1-FrM1 Wetting and Dissociation of Water on Cu(111) and Cu(110)***, **T. Schiros**, H. Öström, K. Andersson, O. Takahashi, L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory

A fundamental understanding of the factors that control the interaction of water metal surfaces is indispensable in predicting electrochemical interactions and pathways for dissociation. Here we address the adsorption of water on Cu(111) and Cu(110) using x-ray absorption and x-ray photoelectron spectroscopy experiments combined with density functional theory calculations. We have found that water adsorbs intact on both surfaces, and wets Cu(110) by forming a monolayer prior to ice formation. In contrast, water does not wet Cu(111), but rather forms three-dimensional ice-like clusters upon adsorption. Our calculations show a much weaker electrostatic interaction and a stronger Pauli repulsion with the oxygen lone pair on Cu(111) compared to Cu(110). We have also investigated how these factors affect the wetting capabilities of water on other metals. We discuss the influence of the d-band density of states with respect to the Fermi level.

8:40am **SS1-FrM2 Point Defects in a Partially Dissociated Wetting Layer: D@sub 2@O/Ru(0001)@footnote 1@***, **P.J. Feibelman**,* Sandia National Laboratories

Ab-initio total energies imply that about 43% of the D@sub 2@O molecules in a first layer on Ru(0001) optimally dissociate to adsorbed OD+D. This compares favorably to new x-ray photoemission measurements,@footnote 2@ which say that (3Â±0.25)/8 of them do. In the optimal wetting layer structure, atop sites on roughly 6% of the outer-layer Ru atoms are available as a natural pathway for D-adatom transport. They represent a surface analog of L-type, Bjerrum defects.@footnote 3@ An equal percentage of the wetting layer's H-bonds, disrupted by the presence of a second D atom, represent the corresponding D-type defects. @FootnoteText@ @footnote 1@ Supported by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is operated by the Lockheed-Martin Company under USDOE Contract No. DE-AC04-94AL85000.@footnote 2@ J. Weissenrieder, A. Mikkelsen, J.N. Andersen and P. J. Feibelman and G. Held (unpublished).@footnote 3@ N. Bjerrum, Kong. Dansk. Vid. Sels.Mat.-fys. Medd. 27, 1(1951).

9:00am **SS1-FrM3 Diffusion of He in Amorphous Solid Water: Observation of an Inverse H/d Lattice Isotope Effect***, **J.L. Daschbach**, G.K. Schenter,* Pacific Northwest National Laboratory*; P. Ayotte,* University of Sherbrooke, Canada*; R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The diffusion of He through amorphous solid water (ASW) has been measured in H@sub 2@O and D@sub 2@O between 50 K and 125 K. He is embedded in a thin layer of ASW grown on Pt(111) at 25 K by molecular beam techniques and subsequently capped with an ASW cap of precise thickness. Linear temperature programmed desorption of the embedded He diffusing through the ASW cap is measured by mass spectroscopy. We find that He diffuses more rapidly in D@sub 2@O than in H@sub 2@O ASW. To our knowledge, this is the first observation of a lattice isotope effect in diffusion. A microscopic kinetic model for He hopping between cage sites in the ASW, reflecting at the Pt(111) interface, and desorbing at the vacuum interface closely fits the data. The diffusion kinetic parameters are found to be D@sub 0@ = 1.3 ± 0.3 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.9 ± 0.17 kJ/mole and D@sub 0@ = 0.8 ± 0.2 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.2 ± 0.17 kJ/mole, for H@sub 2@O and D@sub 2@O respectively. The origin of this inverse isotope effect in the host lattice has been studied using transition state theory. These results indicate the inverse isotope effect arises predominantly from the frustrated rotations of the lattice water molecules.

9:20am **SS1-FrM4 H@sub 2@O/D@sub 2@O Dimer Formation on Pd (111) Studied by STM***, **E. Fomin**, M. Tatarkhanov,* University of California at Berkeley*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We have studied the adsorption and dynamics of H@sub 2@O and D@sub 2@O molecules and dimers on Pd(111) using variable low temperature (@>=@ 25 K) scanning tunneling microscopy (STM). At higher temperatures (>35K) dimers are formed by thermally activated diffusion. At lower temperatures dimer formation was induced by inelastic ecletron tunneling. We measured the hopping rate of single molecules and dimers and discovered that diffusion coefficients differ by 4 orders of magnitude. Recent theoretical analysis@footnote 1@, proposed to explain this effect implies isotopic change in a diffusion coefficient for D@sub 2@O dimers compared to H@sub 2@O ones. In our experiments we were unable to detect this difference. @FootnoteText@ @footnote 1@Ranea VA. Michaelides A. Ramirez R. de Andres PL. Verges JA. King DA. Water dimer diffusion on Pd{111} assisted by an H-bond donor-acceptor tunneling exchange - art. no. 136104. [Article] Physical Review Letters. 9213(13):6104, 2004 Apr 2.

9:40am **SS1-FrM5 Ultrafast Electron Solvation Dynamics and Structure of the Water/Metal Interface***, **M. Wolf**,* Free University Berlin, Germany **INVITED**

The dynamics of excess electrons in water is of fundamental importance for charge transfer and solvation processes in chemistry and biology. We have studied the ultrafast dynamics of photoinjected electrons into thin layers of amorphous ice grown on metal surfaces (Cu(111) and Ru(0001)) and probe the subsequent electron localization, solvation and transfer processes by femtosecond time- and angle-resolved photoemission spectroscopy.@footnote 1@ The solvation dynamics is observed directly through a transient increase of the electron binding energy, which occurs on a 100 fs to 1 ps time-scale and depends critically on the structure of the ice. On the other hand, exceptionally long-lived and highly localized electrons are formed in crystalline ice. As the structure of the solvent can be modified in a controlled way by the growth conditions and substrate our approach provides insights on the relation between structure and solvation dynamics in low dimensional systems. We have also used vibrational sum-frequency generation (SFG) spectroscopy, isotope scrambling experiments and work function measurements to investigate the structure of D@sub 2@O on Ru(0001).@footnote 2@ Our results suggest that the first bilayer consists of intact water molecules, while density functional theory predicts a half-dissociated structure as energetically most favourable state.@footnote 3@ Some explanations for these controversial findings will be discussed. @FootnoteText@ @footnote 1@C. Gahl et. al, Phys. Rev. Lett. 89, 107402 (2002); U. Bovensiepen et al., J. Phys. Chem. B 107, 8706 (2003); Israel. J. Chem. (in press)@footnote 2@D.N. Denzler et al, Chem. Phys. Lett. 376, 618 (2003).@footnote 3@P.J. Feibelman, Science 295, 99 (2002).

10:20am **SS1-FrM7 Interfacial Segregation of Halogen Ions in Alkali Halide Solutions***, **S. Ghosal**,* University of California, Irvine*; B.S. Mun, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; J.C. Hemminger,* University of California, Irvine

In recent years Molecular Dynamics (MD) Simulations@footnote 1, 2@ of alkali halide solutions have predicted the surface segregation of polarizable halogen ions. This is of particular interest since the composition of the liquid/vapor interface of salt solutions has implications for heterogeneous atmospheric chemistry involving sea salt aerosols@footnote 3@. We present here results from our studies of the surface composition of saturated salt solutions. Using a novel high pressure photoelectron spectroscopy (HPPES) system at beamline 9.3.2 of the ALS synchrotron radiation source, we have compared the surface composition of KBr and NaCl crystals cleaved in vacuum with the surface composition of the saturated solutions formed at the deliquescence point, in equilibrium with water vapor. Our results show that the anion/cation ratio in the saturated solution is significantly enhanced within one nanometer of the surface. This is consistent with the predictions of Jungwirth et al@footnote 1, 2@ regarding halogen surface segregation. @FootnoteText@ @footnote 1@ Jungwirth, P.; Tobias, D. J. J. Physical Chemistry 2002, 106(2), 379.@footnote 2@ Jungwirth, P.; Tobias, D. J. J. Phys. Chem. B 2002, 106, 6361.@footnote 3@ Finlayson-Pitts, B. J.; Hemminger, J. C. J. Phys. Chem. 2000, 104(49), 11463 .

10:40am **SS1-FrM8 Measurements of Interfacial Water Properties as a Function of Surface Functionalization Using the IFM***, **G.E. Thayer**,* Sandia National Laboratories, US*; A.K. Boal, B.I. Kim, J.E. Houston, B.C. Bunker,* Sandia National Laboratories

Water exhibits dramatically different structures and properties near interfaces, impacting a wide range of activities including the assembly and properties of nano- and bio-materials, microfluidic and sensor systems. In this work, we use the interfacial force microscope (IFM) to study forces generated by hydrophobic/hydrophilic surfaces in contact with water and the resulting properties of the near-surface water region. The IFM measures force-distance curves between a scanning probe tip and substrate surfaces, providing quantitative measurements of adhesion, long-range (electrical double layer) and short-range (Van der Waals and hydration) forces, and fluid properties such as viscosity. Measurements are performed at the water-solid interface as a function of surface and tip functionalization using self-assembled monolayers (SAMs), temperature, speed, and tip size. Our results indicate that in extreme cases a viscous water layer can form which extends greater than 5 nm from the surface is 6 orders of magnitude more viscous than bulk water. This remarkable effect is due to the interaction of surface hydration forces with the hydrogen-bonding network of water. Such forces are capable of controlling phenomena such as protein adsorption, for example we find forces generated by ordered interfacial water are large enough to resist adsorption of the motor protein kinesin.

11:00am **SS1-FrM9 Light-Induced Contact Angle Switching on Nanowire Surfaces***, **S.T. Picraux**, R. Rosario, T. Clement, J.L. Taraci, J.W. Dailey, D. Gust, A.A. Garcia, M. Hayes,* Arizona State University

We combine monolayer surface chemistry with silicon nanowire substrates to create a lotus leaf like surface, and for the first time demonstrate the amplification of light-induced water contact angle switching. Si nanowires are grown by the vapor-liquid-solid growth technique and the air oxidized surfaces are functionalized with tert-butyldiphenylchlorosilane and perfluorooctyltrichlorosilane, followed by 3-aminopropyldiethoxymethylsilane, to which a photochromic spiropyran molecule was attached. Measurements of the contact angle for water on both the smooth and nanowire surfaces allow direct estimation of the effects of surface morphology on hydrophobicity. Functionalized nanowire surfaces with contact angles above 90° on the smooth surface exhibit superhydrophobic behavior, whereas those with smooth surface angles below 90° exhibit superhydrophilic behavior. Spiropyran-functionalized surfaces show reversible photoswitching of the contact angles. When irradiated with UV light (366nm) the spiropyran is converted from a closed, nonpolar form to a highly polar open form. Visible light (450-550 nm) irradiation of the spiropyran coating yields a relatively hydrophobic surface (higher contact angle) that can be reversibly converted into a more hydrophilic surface (lower contact angle) with UV light irradiation. The nanowire surfaces are observed to exhibit a significant amplification in the contact angle change over that for smooth surfaces (from 12° to 23°). The roughness induced amplification of contact angle switching was accurately predicted using a Wenzel model for contact angles on fractal surfaces. These results, based on a biomimetic approach to nanotechnology, have wide ranging implications for the design of microfluidic systems.

11:20am **SS1-FrM10 Interaction of Glycine with Ice Nanolayers@footnote *@***, **G. Tzvetkov**, M.G. Ramsey, F.P. Netzer,* University of Graz, Austria

The interaction of amino acids with ice surfaces is of interest in a variety of scientific disciplines, ranging from the chemistry in interstellar space and in stratospheric clouds to processes in the geosphere and biosphere. Thin films of ice grown on crystalline substrates under ultrahigh vacuum conditions have been recognised as excellent model systems to study the surface chemistry of molecules on ice. Here we report a study of the interaction of glycine, the simplest amino acid, with ultrathin films of amorphous and polycrystalline ice, as obtained by TPD, XPS, and work function measurements. Thin ice films (@<=@50 layers) have been condensed at 110 K and at 150 K on a hydrophilic single crystalline aluminium oxide surface to produce nanolayers of low-density amorphous and polycrystalline cubic ice, respectively. Glycine overlayers have been prepared by physical vapour deposition at 110 K onto the ice surfaces and mixed glycine-ice layers by codeposition of water and glycine. Whereas the TPD of glycine at 300-350 K remains unaltered by its previous history on ice, the desorption kinetics of water in the temperature range 155-200 K is significantly influenced by the presence of glycine on the ice surfaces, with TPD peaks shifting to lower and higher temperatures with respect to those from the pristine ice surfaces. It is proposed that, on the one hand, the glycine molecules restrict the crystallisation tendency of amorphous to crystalline ice at around 140-160K, and that, on the other hand, the glycine overlayers stabilise the ice surface. The N 1s XPS spectra of the glycine molecules in the monolayer show evidence of a H-bonding interaction of the glycine amino groups with the surface O-H species. The work functions of pristine amorphous and crystalline ice surfaces and the work function changes during glycine adsorption are reported and discussed. @FootnoteText@ @footnote *@ Supported by the Austrian Science Funds.

11:40am **SS1-FrM11 H@sub 2@O-Induced Instabilities at Alumina Surfaces Under Non-UHV Conditions***, F. Qin, N.P. Magtoto,* ***J.A. Kelber,*** University of North Texas*; D.R. Jennison,* Sandia National Labs

We report that ordered, transitional phase Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al single crystal substrates undergo dramatic reorganization and morphological changes upon exposure to H@sub 2@O under non-UHV conditions at room temperature. Notably, the reconstruction does not involve the formation of an UHV-stable hydroxide. STM, AES, LEED and XPS have been used to probe the reactivities of 7 Å - 20 Å thick, ordered Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al(110) and on Ni@sub 3@Al(111) substrates for 10@super-8@ Torr < P@sub H2O@ < 1 Torr at 300 K. STM near-atomic resolution image of the surface of an as-grown Al@sub 2@O@sub 3@/Ni@sub 3@Al(110) oxide film (estimated thickness, ~ 7 Å) indicates a 10 Å repeat distance between rows, in excellent agreement with the results of a first-principles DFT calculation of an ultrathin kappa-phase film. LEED pattern of this film with a 2 x 1 unit cell confirms this structure. Both films are inert toward H@sub 2@O under UHV conditions. We demonstrate that (a) both films undergo severe surface reorganization to a rough, irregular morphology upon exposure to H@sub 2@O at pressures above 10@super-5@ Torr, 300 K, although Al(OH)@sub 3@ formation is only observed above 1 Torr, as predicted by thermodynamics and observed on sapphire(0001); (b) the film grown on the (110) substrate (Al@sub2@O@sub 3@/Ni@sub 3@Al(110)) is significantly more sensitive to H@sub 2@O vapor than the Al@sub 2@O@sub 3@/Ni@sub 3@Al(111) film, and this may be due to the incommensurate nature of the oxide/Ni@sub 3@Al(110) interface; (c) the degree of reconstruction increases with time at constant P@sub H2O@; (d) bias-dependent STM indicates that this reaction is initiated at surface terrace sites, rather than at defect sites or by diffusion to the interface; and (e) the reaction is pressure-dependent, rather than exposure-dependent, indicating that this reaction is cooperative in nature.

Surface Science
Room 210C - Session SS2-FrM
Bimetallic Surface Chemistry and Structure

Moderator: C.M. Byrd, Naval Research Laboratory

9:00am **SS2-FrM3 Tuning the Electronic and Chemical Properties of Bimetallic Surfaces***, **J.G. Chen**, J.R. Kitchin, N.A. Khan, M.A. Barteau,* University of Delaware **INVITED**

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. However, it is difficult to know a priori how the chemical properties of a particular bimetallic surface will be modified relative to the parent metals. There are two critical factors that contribute to the modification of the chemical properties of a metal in a bimetallic surface. First, the geometry of the bimetallic structure is typically different from that of the parent metals, e.g. the average metal-metal bond lengths change. This gives rise to strain effects that are known to modify the electronic structure of the metal through changes in orbital overlap. Second, the presence of other metals around a metal atom also changes its electronic environment, giving rise to further modifications of its electronic structure through the ligand effect. We have investigated the electronic and chemical properties of model bimetallic surface structures, epitaxial monolayers and subsurface epitaxial monolayers, using a combination of experimental and theoretical modeling to gain further insights into these factors. In the current presentation we will first utilize the adsorption and desorption of hydrogen to demonstrate the correlation between the hydrogen binding energy and the center of the d-band in various bimetallic surfaces. We will also provide a general equation that allows one to predict how the electronic properties, especially the d-band center, will be affected in bimetallic systems. We will then use the hydrogenation of cyclohexene to demonstrate the effect of weakly-bonded hydrogen on the novel low-temperature hydrogenation activities on the bimetallic surfaces. Finally, we will use the results from the hydrogenation of cyclohexene to demonstrate a strong correlation between UHV studies on model bimetallic surfaces and reactor studies on corresponding supported bimetallic catalysts.

9:40am **SS2-FrM5 The Study of Electronic Structures and Surface Segregation of Pt@sub 3@M Alloy (M= Ti, V, Cr, Mn, Fe, Co, Ni, and Zr)**, ***B.S. Mun,*** Lawrence Berkeley National Laboratory*; M. Watanabe,* Lawrence Berkeley National Laboratory & SPring-8 Project Team (RIKEN)*; V. Stamenkovic, N.M. Markovic, P.N. Ross Jr.,* Lawrence Berkeley National Laboratory

The systematic study of surface electronic structures of Pt@sub 3@M (M= Ti, V, Cr, Mn, Fe, Co, Ni, and Zr) polycrystalline alloys are presented with high resolution photoemission spectroscopy. The positions of local d-band center from valence band density of state (DOS) measurements are carefully monitored before and after annealing process. Concurrently, the presence and magnitude of surface segregation are measured with angle resolved core-level photoemission spectroscopy. The correlation between the d-band center of DOS and its chemical properties are discussed.

10:20am **SS2-FrM7 The Study of Electronic Structures and Surface Segregation of Single Crystalline Pt@sub 3@Ni(100),(100),and (111)**, ***M. Watanabe****, B.S. Mun, V. Stamenkovic, N.M. Markovic, P.N. Ross Jr.,* Lawrence Berkeley National Laboratory

The surface electronic structures of Pt@sub 3@Ni(100), (110), and (111) single crystalline samples are investigated with synchrotron-based photoemission spectroscopy. From the measurement of valence band spectrum, the d-band centers of density of state are estimated and compared before and after the annealing treatment. In addition, the core-level angle resolved photoemission technique is applied to estimate the segregation of Pt and Ni at the surface. The correlation between electronic structures of each index and its chemical properties are discussed.

10:40am **SS2-FrM8 Chemisorption and Quantum Size Effects on Pseudomorphic fcc-Co and fcc-Fe Films Grown on Cu(100)**, ***H. Yao****, A.G. Danese,* Rutgers University*; C.J. Bosco, F.G. Curti,* Seton Hall University*; R. 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 due to high reflectivity scattering at the film's interfaces forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we have examined the role of MQW states in the chemisorption of CO on Cu MQW overlayers on pseudomorphic fcc-Co and fcc-Fe films grown on Cu(100). In the current work, we report on the adsorption properties of the pseudomorphic transition metal layers themselves. In addition to the fact that the pseudomorphic films represent metastable structures, these systems have partially filled d-bands that change significantly as a function of film thickness. For a Co film with an approximate coverage of 5 monolayers of Co we find that a saturation dosage of CO leads to the formation of a c(2x2) structure as observed in low energy electron diffraction. Inverse photoemission spectra of this system exhibits a two peaked structure centered at 3.8 eV above the Fermi level and is assigned to the unoccupied CO 2@pi@* orbital. CO is found to adsorb molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 400 K, a temperature in the range previously seen for CO adsorbed on hcp Co surfaces. For saturation doses carried out at lower temperatures we find a second lower temperature desorption peak around 270 K in the desorption spectra. These results, and those from fcc-Fe, are compared to the parent single crystal systems.

11:00am **SS2-FrM9 Probing the Mechanism of n-hexane Dehydrocyclization over Pt-Sn Catalysts: Adsorption and Reactivity of n-hexane, 1-hexene, and 1,5-hexadiene on Pt(111) and Sn/Pt(111) Surface Alloys**, ***H. Zhao****, B.E. Koel,* University of Southern California

Supported bimetallic platinum catalysts are widely used to carry out skeletal reactions of alkanes, and such processes including dehydrocyclization are important for naphtha reforming. In order to clarify discussions of the mechanisms of these reactions, we have investigated the adsorption of n-hexane and the reactivity of several likely intermediates in such processes, i.e., 1-hexene and 1,5-hexadiene on well-defined, single-crystal surfaces of Pt(111) and two, ordered Sn/Pt(111) alloys under UHV conditions by using primarily TPD, AES, and LEED. Alloying caused a small decrease in the adsorption energy for all adsorbates. However, alloying decreased strongly the reactivity of 1-hexene and 1,5-hexadiene such that no dehydrogenation occurred during TPD on the (@sr@3*@sr@3)R30°-Sn/Pt(111) alloy with @THETA@@sub Sn@=0.33. This alloy surface does not contain pure-Pt 3-fold sites which can be inferred to be particularly reactive sites. Alloying did not decrease the saturation coverage of any of these molecules.

11:20am **SS2-FrM10 Experimental and Theoretical Characterization of the Structure of Defects at the Pyrite FeS2 (100) Surface**, ***K. Andersson****, M. Nyberg,* Stockholm University, Sweden*; O. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; D. Nordlund,* Stockholm University, Sweden*; T. Kendelewicz, C.S. Doyle, G.E. Brown, Jr,* Stanford University*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford University

Defect-free pyrite FeS2 (100) surfaces were generated and a controlled manipulation of sulfur defect density at these surfaces was performed. Sulfur species of different coordination and environments at the surface were probed by S 2p photoemission in combination with theoretical modeling of S 2p core-level shifts. A strict structural assignment of S 2p peaks at the FeS2 (100) surface in the low defect density regime was achieved. Based on our results, a defect that is related to a surface sulfur vacancy is confirmed to provide the active site for the rapid initial oxidation stage at the pyrite surface.

11:40am **SS2-FrM11 H@sub 2@S Adsorption and Dissociation on Fe-Al and Fe-Si Alloy Surfaces from First Principles**, ***D.E. Jiang****, E.A. Carter,* UCLA

H@sub 2@S attacks iron aggressively and causes the formation of iron sulfide. The sulfidation process is more kinetically favorable than other processes such as carburization. We are interested in determining a way to chemically pretreat iron surfaces to improve resistance to H@sub 2@S. One strategy is to alloy the surface. Here we investigate whether alloying an Fe surface with Al or Si might improve such resistance, via periodic density functional theory calculations of H@sub 2@S adsorption and dissociation on low-index surfaces of the intermetallic compounds FeAl and Fe@sub 3@Si. Stable adsorption structures and relative stabilities of H, S, HS, and H@sub 2@S on FeAl(110), FeAl(100), Fe@sub 3@Si(110), and Fe@sub 3@Si(100) are elucidated and compared with those on Fe(110) and Fe(100). We also present predicted minimum energy paths and energy barriers for the sequential dehydrogenation steps: H@sub 2@S to HS + H and HS to H + S. Our study shows that FeAl is indeed more resistant to H@sub 2@S attack than Fe, while Fe@sub 3@Si is as susceptible as Fe.

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