

Sunday Afternoon, October 30, 2005

Topical Conference on Renewable and Alternate Energy Room 304 - Session EN-SuA

Renewable and Alternate Energy

Moderators: R. Ahrenkiel, University of Denver, G. Parsons, North Carolina State University

3:00pm EN-SuA1 Scientific Challenges in Sustainable Energy Technology, **M.S. Lewis**, California Institute of Technology **INVITED**

This presentation will describe and evaluate the challenges, both technical, political, and economic, involved with widespread adoption of renewable energy technologies. First, we estimate the available fossil fuel resources and reserves based on data from the World Energy Assessment and World Energy Council. In conjunction with the current and projected global primary power production rates, we then estimate the remaining years of supply of oil, gas, and coal for use in primary power production. We then compare the price per unit of energy of these sources to those of renewable energy technologies (wind, solar thermal, solar electric, biomass, hydroelectric, and geothermal) to evaluate the degree to which supply/demand forces stimulate a transition to renewable energy technologies in the next 20-50 years. Secondly, we evaluate the greenhouse gas buildup limitations on carbon-based power consumption as an unpriced externality to fossil-fuel consumption, considering global population growth, increased global gross domestic product, and increased energy efficiency per unit of globally averaged GDP, as produced by the Intergovernmental Panel on Climate Change (IPCC). A greenhouse gas constraint on total carbon emissions, in conjunction with global population growth, is projected to drive the demand for carbon-free power well beyond that produced by conventional supply/demand pricing tradeoffs, at potentially daunting levels relative to current renewable energy demand levels. Thirdly, we evaluate the level and timescale of R&D investment that is needed to produce the required quantity of carbon-free power by the 2050 timeframe, to support the expected global energy demand for carbon-free power. Fourth, we evaluate the energy potential of various renewable energy resources to ascertain which resources are adequately available globally to support the projected global carbon-free energy demand requirements. Fifth, we evaluate the challenges to the chemical sciences to enable the cost-effective production of carbon-free power on the needed scale by the 2050 timeframe. Finally, we discuss the effects of a change in primary power technology on the energy supply infrastructure and discuss the impact of such a change on the modes of energy consumption by the energy consumer and additional demands on the chemical sciences to support such a transition in energy supply.

3:40pm EN-SuA3 Our Solar Power Future: The U.S. PV Industry Roadmap for 2030 and Beyond, **A.M. Barnett**, University of Delaware; **R. Resch**, Solar Energy Industries Association **INVITED**

The next 10 years are critical for worldwide solar power development. Actions by industry and government will determine whether solar power is catapulted to a new level and whether the United States will regain its position at the forefront of solar power development. Investment decisions over the next decade for research, new manufacturing, and creating new markets will determine where solar power will thrive and where it will merely survive. Solar power can provide great value in residential and commercial grid-connected applications, for individual consumers and businesses, as well as for utilities and the communities they serve. Our goals for 2030 are solar power system costs of \$2.33 per watt, solar electricity prices of 3.8 cents per kilowatt-hour (kWh) delivered to the customer, installed solar power generation of 200 gigawatts (GW), and direct employment of 260,000 people.

4:20pm EN-SuA5 Hydrogen and Chemicals from Fossil and Renewable Fuels by Autothermal Reforming, **L.D. Schmidt**, University of Minnesota **INVITED**

Autothermal reactors have great promise for hydrogen and chemicals production because they have reactor residence times of 10-3 seconds and require very simple reactors. We describe the production of hydrogen and olefins from fossil fuels from methane to diesel and from renewable fuels such as ethanol and biodiesel in millisecond reactors. For successful vaporization and mixing of heavy fuels the use of fuel injectors for rapid vaporization and mixing is essential to suppress flames and carbon formation. For ethanol to hydrogen we obtain 80% selectivity to hydrogen at nearly 100% conversion of ethanol and oxygen for an ethanol-air feed. By adding water we obtain 110% (H₂ from ethanol and water) in a single

stage reactor and 130% H₂ selectivity in a staged reactor where a cooler section undergoes the water gas shift reaction. For biodiesel (the methyl ester of C18 fatty acids from soy oil), we can obtain 80% H₂ selectivity at C/O=0.8 and 80% selectivity to olefins at C/O=1.5. At higher C/O ratios the ester linkage also survives to produce olefinic esters. Modeling with detailed surface and homogeneous chemistry is used to simulate and understand these processes.

5:00pm EN-SuA7 Fuel Cells from the Viewpoint of a Skeptical Optimist, **T. Zawodzinski**, Case Western Reserve University **INVITED**

Fuel cells have been the subject of hype and backlash of late. The hype took various forms, including the 'We'll have a product next year' variety as well as inflated estimates system efficiency, simplicity, etc. Hopes have been dashed because of failure to adequately anticipate the difficulty of some technical and practical problems and from the short duration over which present-day configurations have been tested. The backlash has evolved from reaction to not meeting promises as well as from the realization of the aforementioned problems. Also, fuel cells are linked in many minds to the Hydrogen Economy, which has its own set of detractors. After reviewing these promises and pitfalls, this talk will discuss the current state of development of fuel cells, highlighting technical state of the art. Significant achievements and substantial activities to address some of the major challenges posed by the combination of cost, reliability and performance/functionality factors will be highlighted. By presenting a realistic assessment of these aspects, we hope to leave people with 'reasons to believe' in the promise of fuel cell technology in some applications

Surface Science

Room 202 - Session SS1-MoM

Catalytic Chemistry of Hydrocarbons

Moderator: M. Trenary, University of Illinois at Chicago

8:20am **SS1-MoM1 Transition States of Hydrogenation and β -Hydride Elimination in Alkyl Groups on the Pt(111) Surface**, P.P. Ye, A.J. Gellman, Carnegie Mellon University

Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups and the transition state to β -hydride elimination in alkyl groups on the Pt(111) surface. Eight different alkyl and fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of their respective alkyl and fluoroalkyl iodides. Co-adsorption of hydrogen and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated to the field and polarizability substituent constants of the alkyl groups in the form of a linear free energy relationship. Increasing both the field and polarizability constants of the alkyl groups increases the barrier to reaction. These substituent effects indicate that the α -carbon in the transition state is cationic with respect to the initial state of alkyl group and that the reactant has greater charge density on the α -carbon than the transition state. In the absence of adsorbed hydrogen, alkyl groups on Pt(111) dehydrogenate via β -hydride elimination. In the fluorinated alkyl groups this then leads to the deposition of hydrogen on the surface and the hydrogenation of the intact fluoroalkyl groups to form fluoroalkanes. The desorption kinetics of the product fluoroalkanes serves as a measure the kinetics of the β -hydride elimination. The field effects of the fluorinated substituents increase the barriers to β -hydride elimination. The interpretation of this effect is that the β -carbon atom in the transition state is cationic with respect to the reactant. This is consistent with observations made on the Cu(111) surfaces although the substituent effect is smaller on the Pt(111) surface indicating a difference in the nature of the transition states on the two surfaces.

8:40am **SS1-MoM2 Surface Science Insights on the Enantioselective Hydrogenation of Activated Ketones on Chirally-Modified Platinum**, S. Lavoie, P.H. McBreen, Université Laval, Canada

The asymmetric hydrogenation of α -ketoesters on chirally-modified platinum catalysts, the Orito reaction, involves a complex set of interrelated interactions. These include the chemisorption of the chiral modifier and the ketoester on the metal surface, as well as the modifier-ketoester interactions responsible for enantiodifferentiation. In order to isolate the key modifier-ketoester interactions, RAIRS studies were performed on a range of aromatic-carbonyl co-adsorption systems of progressively increasing complexity. All effective modifiers for the Orito reaction contain both an extended aromatic function and a function capable of conventional H-bonding. It is generally accepted that the aromatic function serves to anchor the chiral modifier to the platinum surface, and that it may also play a steric role in inducing asymmetry. However, evidence will be presented for a key additional role for the aromatic anchor. Using results for the Pt(111) surface, it will be shown that the modifier-ketoester interaction may be described in terms of two distinct H-bonds, one of which is to the chemisorption activated aromatic system. It will be shown that such a two-point H-bonding interaction can account for most observations in the catalysis literature concerning the Orito reaction.

9:00am **SS1-MoM3 Electronic States of Adsorbed Molecules and Vibrational Excitation by Inelastically Tunneled Electrons from STM Tip**, M. Kawai, RIKEN and University of Tokyo, Japan

INVITED

The inelastic tunneling process of electrons between the tip of an STM and the target molecule can lead to various dynamical processes at surfaces such as desorption, lateral hopping, rotation and chemical reaction via the excitation of vibrational modes of adsorbed molecules. The vibrational mode that are excited through the process could be defined through the response of the molecular motion to the applied bias voltage, i.e. action spectrum. Action spectra for hopping motion of cis-2-butene on Pd(110), cleavage of dimethyl-disulfide on Cu(111) and hopping motion of cleaved product methyl-thiol show clear thresholds in bias voltage that are equivalent to certain vibration modes, the excitation mechanism of which can be understood by the resonant tunneling mechanism. When the

electron jumps into or out of a certain molecular orbital, molecules will temporarily go through the negative or positive ion state. And vibration states can be excited, during the relaxation process. Inelastic process that leads to vibrational excitation has attracted much attention of since the conductivity of molecules bridging the electrodes is found to be strongly affected when they are vibrationally excited. Considering that the conduction electrons passes through the electronic state crossing the Fermi level or hopping through the HOMO or LUMO state of the molecule, the electronic state of adsorbate should play a crucial role in the molecular electronics as well as the chemical reactions at surfaces.

9:40am **SS1-MoM5 The Reaction Pathway for the Synthesis of Vinyl Acetate on Pd(111)**, W.T. Tysoe, F. Calaza, D. Stacchiola, UW-Milwaukee

The palladium-catalyzed synthesis of vinyl acetate from acetic acid, ethylene and oxygen is studied on Pd(111) single crystal surfaces. The rate of reaction between gas-phase ethylene and adsorbed acetate species is followed using infrared spectroscopy by measuring the time dependence of the intense OCO acetate mode at 1414 cm⁻¹. The acetate removal kinetics are modeled by assuming that ethylene adsorption is blocked by acetate species. Temperature-programmed reaction confirms that vinyl acetate is formed in the reaction. The reaction pathway is explored by comparing the reaction rates of d₂, 1,1-d₂, 1,2-d₂ and normal ethylene with surface acetates. d₂ ethylene reacts about six times more slowly than C₂H₄ indicating that hydrogen is involved in the rate-limiting step. The reaction rates are different for 1,1-C₂H₂D₂ and 1,2-C₂H₂D₂. This indicates that vinyl acetate formation occurs via the insertion ethylene into the surface acetate species to form an acetoxyethyl-palladium intermediate, which then reacts to form vinyl acetate via a β -hydride elimination reaction, rather than by vinyl formation and addition to the acetate species to form vinyl acetate. The different reactivities of the isotopomers is rationalized by making the reasonable assumption that ethylene adsorption is blocked by the acetoxyethyl-palladium intermediate. When reaction is carried out using 1,1-C₂H₂D₂, the intermediate can be formed with exclusively deuterium atoms in the β -position, slowing its rate of decomposition, blocking ethylene adsorption, and slowing the reaction rate. Reaction with 1,2-C₂H₂D₂ results in one hydrogen being in the β -position, allowing it to decompose more rapidly. Final conformation of this pathway comes from detecting the acetoxyethyl-palladium intermediate using infrared spectroscopy when reaction is carried out using C₂H₄.

10:00am **SS1-MoM6 Vinyl Acetate Synthesis on Pd-based Catalysts: Structure Sensitivity and Active Site Identification**, D. Kumar, M.S. Chen, Y.F. Han, C.-W. Yi, K. Luo, D.W. Goodman, Texas A&M University

The synthesis of vinyl acetate (VA) is a very important industrial reaction and is produced by acetoxylation of ethylene over Pd-Au catalysts. Historically this highly selective reaction has been studied using conventional kinetic techniques; however, there is no consensus regarding a reaction mechanism. A combination of surface science techniques and kinetic measurements has been used in the current study to address the structure sensitivity and the active ensemble for the reaction. VA synthesis was carried out over Pd and Pd-Au high-surface-area and model planar catalysts and the reaction rates found to be: Pd(100) < 5 wt% Pd/SiO₂(d_{Pd}=4.0nm) < 1 wt% Pd/SiO₂(d_{Pd}=2.5nm). A particle size dependence of the reaction rates implies a degree of structure sensitivity. Furthermore, the addition of Au to Pd/SiO₂ catalysts leads to a significant increase in the reaction rate and selectivity with the latter related directly to a change in the reaction order with respect to ethylene. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd/Au(100) and Pd/Au(111) confirms that Pd is present as isolated monomers on a Au-rich surface. A pair of Pd monomers is the optimum active site for the adsorption of ethylene and acetate species, and leads to the formation of VA. The spacing between the two active Pd monomer pairs is crucial on Au(100) and Au(111), evident by the relative rates of VA synthesis on Pd/Au model catalysts, i.e. Pd/Au(111) < Pd/Au(100).

10:20am **SS1-MoM7 Selective Oxidation of Hydrocarbons on Chemisorbed Oxygen Covered Au(111)**, X. Deng¹, C.M. Friend, Harvard University

Chemisorbed oxygen covered Au(111) has been found to be active for the partial oxidation of hydrocarbons. Specifically, chemisorbed oxygen on a herringbone-Au(111) was deposited via electron-induced dissociation of NO₂. Several hydrocarbons, including cyclohexene and styrene, were

¹ Morton S. Traum Award Finalist

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studied on the O/Au surface by using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The primary products are styrene epoxide and benzene for styrene and cyclohexene oxidation, respectively. HREELS was performed to identify the intermediates of the reactions. In combination with the observed isotope effects, the reaction mechanisms on O/Au(111) were proposed and compared with those on O/Ag(110).

10:40am **SS1-MoM8 Reactivity Studies of Molybdenum Carbide Nanoparticles formed on Au(111) using Reactive-Layer Assisted Deposition**, *D.V. Potapenko*, BNL; *J.M. Horn, M.G. White*, BNL and SUNY at Stony Brook

The chemical properties of MoC@sub x@ nanoparticles prepared by a novel method on the Au(111) support have been studied using cyclohexene, cyclohexane and benzene as test molecules. The surfaces have been prepared by depositing Mo by physical vapor deposition (PVD) on a reactive layer of ethylene, which was physisorbed on a Au(111) substrate at low temperatures (85 K). STM imaging shows that the resulting MoC@sub x@ particles have a narrow size distribution and preferentially nucleate near the 'elbow' sites on the reconstructed (22 x @sr@3)-Au(111) surface. Auger and XPS indicate that the MoC@sub x@ particles are near stoichiometric (x = 1). Also we have found that in the thermodynamically stable state MoC@sub x@ particles are partially encapsulated by gold from the support. Thermal programmed desorption (TPD) studies have shown that cyclohexene undergoes three different reactions on bare (not encapsulated by Au) MoC@sub x@ nanoparticles: hydrogenation to cyclohexane, partial dehydrogenation with benzene formation, and complete dehydrogenation with surface carbon deposition. In contrast, interaction of cyclohexene with Au-encapsulated MoC@sub x@ nanoparticles exhibits a very high (at least 95 %) selectivity toward partial dehydrogenation to benzene. The found selectivity is higher than that for cyclohexene reactions on either C/Mo(110) or Pt(111) surfaces. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract No. DE-AC02-98CH10886.

11:00am **SS1-MoM9 The Mechanism of Partial Oxidation of Styrene on Ag(111)**, *A. Klust, R.J. Madix*, Stanford University

The partial oxidation of olefins on Ag surfaces has been a long standing problem in surface science and is of great commercial interest. In particular, the nature of reaction intermediates has been subject of intense debate. One candidate for the reaction intermediate is the oxametallacycle where both ends of a -C-C-O- chain are attached to the Ag surface (see e.g. [1]). We present a temperature programmed reaction spectroscopy (TPRS) and x-ray photoelectron spectroscopy (XPS) study of the partial oxidation of styrene on Ag(111). The reaction products are CO@sub 2@, H@sub 2@O, styrene oxide, benzene, and benzoic acid. XPS gives evidence for two different intermediate structures that we assign to an oxametallacycle and to benzoate. The oxametallacycle seems to be the precursor for the formation of the styrene oxide as well as for the formation of the benzoate while the benzoate itself leads to the formation of CO@sub 2@, benzene, and benzoic acid. The results are explained in the framework of a model based on the asymmetry of the oxametallacycle caused by the phenyl ring of styrene. @FootnoteText@ @footnote 1@ S. Linic and M. A. Barteau, J. Am. Chem. Soc. 125 (2003) 4034.

11:40am **SS1-MoM11 Catalytic Hydrodechlorination of Chlorobenzene and Chlorotoluene Isomers on the Pt(111) Surface**, *B.M. Haines*, University of Michigan; *D.A. Fischer*, National Institute of Standards and Technology; *J.L. Gland*, University of Michigan

The catalytic hydrodechlorination of chlorobenzene on the Pt(111) surface has been characterized using temperature programmed reaction spectroscopy (TPRS) and fluorescence yield near edge spectroscopy (FYNES) above the carbon K edge. Thermal hydrodechlorination, dehydrogenation and rehydrogenation result in the formation of benzene, HCl, and H@sub 2@ when chlorobenzene is heated on platinum. The effects of methyl substituents on hydrodechlorination were probed using the isomers of chlorotoluene. The chlorobenzene monolayer adsorbs on the Pt(111) surface with the plane of the ring at a 45° angle from the surface as indicated by FYNES. The monolayer partially desorbs at 196 K and the remaining chlorobenzene then undergoes dechlorination via two reaction channels at 270 K and at 420 K as shown by TPRS. Comparison of the integrated peak areas for these two channels yields a 3:2 (270 K: 420 K) ratio. Temperature programmed-FYNES show that a stable cyclohexadiene intermediate is formed above 250 K that is coadsorbed in a 3:2 ratio with molecular chlorobenzene. The remaining molecular chlorobenzene is

dechlorinated in the 420 K range to form additional adsorbed cyclohexadiene. For chlorotoluene, substituent effects dominate activation of the C-Cl bond through the ring and dehydrogenation of the methyl group at low temperatures.

Surface Science

Room 203 - Session SS2-MoM

Oxide Surface Structure and Characterization

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

8:40am **SS2-MoM2 Thermodynamic Stability of Alumina Films on NiAl(110) and the Dynamics of Their Extended Defects**, *K.F. McCarty, N.C. Bartelt, J.P. Pierce*, Sandia National Laboratories; *C.B. Carter*, University of Minnesota

A well-studied oxide surface is the thin-film alumina formed by oxidizing a NiAl(110) surface [J. Libuda et al., Surf. Sci. 318 (1994) 61]. Here, we show how low-energy electron microscopy (LEEM) can determine the thermodynamic stability of these alumina films and image the formation and time evolution of extended crystallographic defects. At sufficiently high temperature, discrete islands of crystalline oxide form when NiAl is exposed to oxygen. Analysis by electron diffraction and scanning tunneling microscopy establish that these oxide islands are the same alumina produced by the literature "recipe." We directly measure the thermodynamic stability (Gibbs formation energy) of the alumina -- at a fixed temperature, the pressure of oxygen in equilibrium with the oxide is determined by finding the pressure at which individual alumina islands neither shrink nor grow. We find that the equilibrium oxygen pressure of the thin-film alumina is many orders of magnitude greater than bulk alumina. Analysis suggests that strain is the cause of the remarkable instability of the alumina film. We also investigate how two types of planar defects in the films, boundaries between rotational and translation domains, originate and evolve. Typically, domains in films are thought to originate from the nucleation stage of film growth. That is, domain boundaries occur where rotated or translated islands impinge. Indeed, we observe that rotational boundaries form in this manner. In contrast, translation ("antiphase") boundaries are observed to nucleate, grow, and even move within isolated oxide islands. The fact that translation boundaries form within isolated alumina islands strongly suggests that the boundaries are introduced to relieve strain. We will discuss how formation of translation domains reduces film strain. 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.

9:00am **SS2-MoM3 Growth and Properties of Vanadia on Anatase TiO@sub 2@ (001) and (101) Surfaces**, *W. Gao*, Yale University; *R. Klie*, Brookhaven National Laboratory; *E.I. Altman*, Yale University

Inspired by its unique catalytic properties and elusive structure, we have been studying the structure of vanadia layers deposited onto epitaxial anatase (001) and (101) films. For anatase (001), a (1x4)/(4x1) reconstruction was observed by reflection high-energy electron diffraction (RHEED) and low energy electron diffraction (LEED). After depositing 1 ML at 525 K, X-ray photoelectron spectroscopy (XPS) showed predominantly V@super 5+@ and the (1x4)/(4x1) diffraction patterns were replaced by (1x1) patterns indicating that vanadia lifts the reconstruction and the monolayer is pseudomorphic. Continued growth caused the RHEED pattern to fade, suggesting that V@sub 2@O@sub 5@ epitaxy cannot be continued beyond 1 ML. At 750 K, however, VO@sub 2@ formed and the (1x1) pattern remained clear for 20 nm of vanadia. At 800 K, a c(2x2) termination was observed. These results suggest that the V@super 5+@ in the monolayer is due to 0.5 ML of terminal oxygen which allows epitaxy and the 5+ oxidation state. These results were compared with those for anatase (101) surfaces, the lowest energy anatase surface. The (101) surfaces were formed by depositing TiO@sub 2@ onto LaAlO@sub 3@(110). Although x-ray diffraction and scanning transmission electron microscopy indicated that the films grew with anatase (102) planes parallel to the interface, RHEED and LEED showed the surface diffraction patterns expected for a (101) surface and STM showed the oblique unit cell of the (101) surface. These conflicting results were attributed to the surface faceting to expose the lowest energy (101) surface. Similar to anatase (001), a (1x1) diffraction pattern is maintained after depositing 1 ML of V@sub 2@O@sub 5@; however, further vanadia deposition led to three dimensional vanadia clusters. STM is being used to further characterize the structure of the vanadia monolayers on the two anatase surfaces.

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9:20am **SS2-MoM4 Oxide Nanolayers: Artificial Phases in Low Dimensions**, *F.P. Netzer, S. Surnev, J. Schoiswohl, G. Parteder, M.G. Ramsey, Karl-Franzens-University Graz, Austria; G. Kresse, University of Vienna, Austria*

Transition metal oxides in ultrathin nanostructured layers on well-defined metal surfaces may form novel oxide phases, that do not occur in nature. These "artificial oxide phases" display new physical and chemical properties, which make them potentially interesting materials for nanotechnology applications. They derive their formation, on the one hand, from the interactions at the interface between the oxide overlayer and the metal substrate and, on the other hand, from kinetic constraints during the growth process. The growth of a variety of novel low-dimensional vanadium, nickel, and manganese oxide structures on Rh and Pd single crystal surfaces has been followed and the surface phase diagrams and the atomic structures of oxide nanolayer phases have been characterised by the interplay of various experimental and theoretical methods (STM, LEED, UPS and XPS, HREELS, ab initio DFT). The influence of energetic and strain effects at the interface is important and determines the particular structures, which are observed on different substrates. The oxide structures to be discussed comprise highly oxidised (nominally $V_{0.3}O_{0.9}$), mixed valent ($VO_{1.6-2.09}$), and reduced (nominally $V_{0.2}O_{0.3}$) vanadium oxide surface phases on Rh(111) and Pd(111) substrates, a $c(4 \times 2)$ wetting layer of an interfacial nickel oxide on Pd(100), which acts as an interlayer to cubic NiO growth, and various manganese oxide phases on Pd(100). It is shown that, in addition to the thickness confinement in the nanolayers, the lateral confinement as imposed by the regular step array on a vicinal substrate surface can promote the growth of novel oxide nanostructures. @FootnoteText@ Supported by the Austrian Science Fonds and the EU STREP Programme GSOMEN.

9:40am **SS2-MoM5 Metal Atoms and Clusters on Oxide Surfaces and Thin Films: Charging Mechanisms and Consequences**, *G. Pacchioni*, Università di Milano-Bicocca, Italy **INVITED**

Metal clusters deposited on oxide surfaces exhibit specific chemical and physical properties often connected to their low dimensionality. The properties of truly nano-clusters a few atoms in size or even of isolated metal atoms are highly depending on the type of oxide support, adsorption site, surface morphology, etc. One of the aspects that can deeply modify the properties of the adsorbed metal atoms or clusters is the occurrence of charge transfers at the metal-oxide interface. Recent studies have shown that charged clusters, and in particular cluster anions, are catalytically more active than their neutral counterparts. Charging mechanisms of metal atoms and clusters on oxide surfaces is the topic of this talk. Using high quality electronic structure calculations in combination with experimental spectroscopic measurements, we will discuss in which conditions charging occurs and how to measure it. The systems considered are metal atoms like Cu, Au, Pd, on oxide substrates like MgO, SiO₂, and TiO₂ single crystals or in polycrystalline or amorphous form. We will show that a major role in charging of the deposited atoms is played by point defects at the oxide surface and discuss methods to prove the occurrence of the charge transfer. In the second part of the talk we will examine methods to induce charging even without implying the presence of defects. In particular, we will consider metal atoms deposited on ultra-thin oxide films epitaxially grown on metal single crystals. We will discuss the adsorption properties of Pd, Ag, and Au atoms on 1 to 5 layers thick films of MgO on Mo(100) and compare them to those of MgO(100) single crystals. On supported MgO thin films charging can occur from the metal substrate to adsorbed atoms with high electron affinities, like Au. We will discuss possible mechanisms for this charge transfer like direct tunneling or dielectric breakdown induced by an external electric field.

10:20am **SS2-MoM7 Growth of WO₃ Clusters on TiO₂(110)-(1x1)**, *O.A. 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

Tungsten oxide clusters supported on Al₂O₃, SiO₂, ZrO₂ and TiO₂ are known to be catalytically active for a wide range of acid-catalyzed reactions including alcohol dehydrogenation, alkane hydrogenation, metathesis etc. In this work, we studied the growth of WO₃ nanoclusters on TiO₂(110)-(1x1) surface using STM. Submonolayer amounts of WO₃ were deposited on TiO₂(110) via direct, thermal evaporation from WO₃. Using XPS we have determined that WO₃ deposited on TiO₂(110) is thermally stable and remains fully oxidized up to 700 K. Atomically resolved studies of WO₃ deposited at room

temperature on TiO₂(110) show only fuzzy, poorly defined features indicating that the clusters are only weakly bound to the substrate. Subsequent annealing to 600 K results in the formation of bright WO₃ clusters that can be easily imaged. In case of low WO₃ coverages (< 0.25 ML) the STM images indicate that the majority of clusters have identical size (~0.6nm in apparent diameter) and position with respect to the substrate registry. The amount of deposited WO₃ from a quartz crystal microbalance measurement together with the observed cluster density yields the upper bound of $x \leq 3$ for the number of W atoms in each cluster. Additionally, annealed WO₃ clusters exhibit preferential alignment across the Ti⁴⁺ rows suggesting attractive interactions between them.

10:40am **SS2-MoM8 Imaging of Atoms on Oxide Surfaces by X-ray Standing Wave Fourier Inversion**, *C.-Y. Kim*, Northwestern University; *J.W. Elam*, Argonne National Laboratory; *D. Goswami, M.J. Bedzyk, P.C. Stair, S. Christensen, M.C. Hersam*, Northwestern University

Supported metal oxides are among the most important of catalytic materials systems. However, there is a lack of experimental atomic-scale structural information for describing the relevant interfaces. We combine atomic layer deposition (ALD) and x-ray standing wave (XSW) atomic-imaging to address this challenge. As a first case, we determine the precise registry of W atoms on a rutile TiO₂(110) surface. XSW results show that tungsten has an average adsorption height of 3.48 Å above the Ti-O plane. The direct-space image reveals that W occupies the Ti-site that would be occupied by Ti if the bulk structure were extended above surface. The tungsten atoms are vertically shifted upward from the ideal Ti-site location by +0.23 Å. We speculate that the sacrificial role of Si₂H₆ in removing surface species may apply to the TiO₂ substrate in addition to the W ALD film. This is the first atomic structure determination of a supported catalytic phase under ambient conditions. The results suggest that supported metal cations locate as if they were the next layer in the bulk structure. The ALD method for supported catalyst material preparation provides a bridge over the "materials preparation gap" that typically separates practical, high-surface-area and single crystal model catalytic materials.

11:00am **SS2-MoM9 Terminal Oxygen Structures on WO₃(100) Thin Films**, *M. Li, A. Posadas, C. Ahn, E.I. Altman*, Yale University

Scanning tunneling microscopy (STM) was used to characterize the surface reconstructions on epitaxial WO₃(100) thin films on LaAlO₃(100) in a reducing environment. As the films were annealed between 600-770 K, a myriad of surface structures related to terminal oxygen were observed. Upon initial reduction the surface was covered with small $c(2 \times 2)$, $p(2 \times 2)$, $c(4 \times 2)$, and poorly ordered terminal oxygen terraces all coexisting with (1x1) islands. Further reduction caused large flat terraces of poorly ordered terminal oxygen to coexist with strand terminated $p(n \times 2)$ terraces with $n = 3-5$. Continued reduction led to a zigzag arrangement on top of the $p(n \times 2)$ surface, half-height $p(2 \times 2)$ and $c(4 \times 2)$ islands, and a local (15x2) structure. The latter three structures could only be explained by crystallographic shearing of the surface plane. In contrast to higher annealing temperatures, the exclusively $p(n \times 2)$ terminated surface characterized by alternating strands and troughs was not observed, suggesting that at lower temperatures crystallographic shear competes with the bulk migration responsible for trough formation as the dominant surface reduction mechanism.

Surface Science

Room 202 - Session SS1-MoA

Catalysis for the Hydrogen Economy

Moderator: G.B. Fisher, Delphi Research Labs

2:00pm SS1-MoA1 In-situ CV and XPS Evaluation of Tungsten Carbides as Alternative Electrocatalysts, M.B. Zellner, J.G. Chen, University of Delaware

The purpose of this research is to examine the feasibility of using tungsten carbides (WC) and platinum modified tungsten carbides (Pt/WC) as direct methanol fuel cell (DMFC) and hydrogen fuel cell electrocatalysts. The motivation to study tungsten carbides stems from the fact that current fuel cells require the use of Pt or Pt/Ru anodes, which are expensive and easily poisoned by CO. The successful development of tungsten carbide electrodes as Pt/Ru substitutes can therefore positively influence the commercialization of DMFC and hydrogen fuel cell systems. Previously, reactions of CH₃OH, H₂O, H₂ and CO over single crystal and physical vapor deposited (PVD) thin film WC and Pt/WC surfaces have been studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The results show that the carbide surfaces possess characteristics critical to application as fuel cell anodes. In particular, these surfaces are highly active toward the decomposition of CH₃OH and H₂O, and are able to desorb CO at relatively low temperatures. Recently, Pt-modified WC films along with PVD thin films of WC and W₂C have been tested for stability in an acidic environment and activity of methanol oxidation using an in-situ cyclic voltammetry (CV)/ X-ray Photoelectron Spectroscopy (XPS) test station. The tests show stability of WC to ~0.8 V wrt. NHE and a synergistic effect at monolayer Pt coverage, resulting in enhanced stability to ~1 V. Additionally, WC and Pt/WC surfaces show methanol O-H and C-H oxidation states, with the Pt/WC surface displaying greater methanol oxidation activity compared to WC or pure Pt foil.

2:20pm SS1-MoA2 Development of a High Temperature Electrochemical Reactor with Differential Electrochemical Mass Spectrometry for Kinetic Rate Analysis of Methanol Oxidation, L.M. Roen, E.M. Stuve, University of Washington

Direct methanol fuel cells have nearly the same potential as hydrogen fuel cells, ~1.2 V, though practical implementation has been limited by the kinetics of methanol oxidation. A full Langmuir-Hinshelwood model was previously developed¹ in order to ascertain the kinetic rates of each elementary step of methanol oxidation on platinum. The strongest criticism of this model was its neglect of partial oxidation products. In addition to the empirical approach, we are collaborating with a theoretical group using Density Functional Theory to predict the kinetics rates from first principles. Experimentally, we need 4 independent measurements at different temperatures to find the kinetic rates and activation energies. The experimental system was designed to meet several requirements: (1) clean electrolyte environment, (2) no loss of potential control between measurements, (3) heating control from room temperature to 95°C, (4) quantitative detection of CO₂, and, (5) minimal time delay for detection of volatile species. We have successfully constructed an electrochemical microreactor with on-chip heating attached to a differential electrochemical mass spectrometer (DEMS) to meet these requirements. Expected results of the measurements are kinetic rate constants, activation energies, and Tafel slopes for five elementary steps in the methanol oxidation process; direct oxidation to CO₂, series oxidation of CO to CO₂, accumulation of the CO intermediate, incomplete oxidation of methanol, and adsorption of methanol; over temperature, potential, and concentration ranges of 22 - 100°C, 0.2 - 0.6 V/rhe, and 0.01 - 5 M respectively. ¹FootnoteText¹ @footnote 1 @ S. Sriramulu, T.D. Jarvi, E.M. Stuve, Reaction mechanism and dynamics of methanol electrooxidation on platinum(111), J. Electroanal. Chem. 467 (1999) 132-142.

2:40pm SS1-MoA3 Hydrogen Production and Conversion, I. Chorkendorff, Center for Individual Nanoparticle Functionality CINF, Denmark INVITED

On many levels there are strong efforts being made to find alternative ways of distributing energy in the future. Hydrogen is considered to be one of the more potential energy carriers. Since there is still a long way to go before we can produce hydrogen in sufficient amounts - and at competitive prices - directly from renewable energy sources, we will still have to rely on fossil fuels for many years to come. The fact that hydrogen, if combined

with carbon dioxide sequestration, can be made from fossil fuel without contributing to the green house effect may be a route of soft transition. Today hydrogen is essentially produced by the so-called steam reforming process of natural gas. In a number of studies we have investigated the fundamental aspects of methane and CO conversion on Ni and Ru surfaces - especially with respect to the effect of structure. From studies of Nitrogen dissociation on Ru we have learned that the so-called B5 sites are simply dominating the reactivity. It is therefore also of interest to investigate how these types of defect sites may influence other reactions - for example those related to the hydrogen production, such as the steam reforming process and its reverse reaction: the methanization reaction. Non-conventional production and conversion of hydrogen are also interesting, particularly because the extensive use of fuel cells will require developing new electrode materials that can replace the expensive and scarce Platinum. We will discuss different routes for development of new electrode materials, involving both screening of alloy materials under well defined conditions combining high pressure cells with conventional UHV equipment, but also biomimetic approaches. The latter involves materials inspired by the active co-factors of nitrogenase and hydrogenase enzymes for electrochemical hydrogen production.¹FootnoteText¹ @footnote 1 @ B. Hinnemann, P. G. Moses, J. Bonde, I. Chorkendorff & J. K. Nørskov, Accepted JACS (2005).

3:20pm SS1-MoA5 The Electronic Structure Effect in Heterogenous Catalysis, A. Nilsson, Stanford University; L.G.M. Pettersson, Stockholm University, Sweden; B. Hammer, University of Aarhus, Denmark; T. Bligaard, C.H. Christensen, J. Nørskov, Technical University of Denmark

Transition metals are used extensively as catalysts and the variation in the catalytic activity for a given reaction is determined largely by the differences in the strength of the adsorbate-surface interaction from one metal to the next. In the following presentation we will demonstrate how we can understand trends in adsorbate-surface interactions based on a particularly simple picture that was originally developed to describe the difference in reactivity for hydrogen dissociation on metal surfaces, the d-band center model.¹Footnote 1 @ We will show that it applies quite generally and in particular we will show that it can be validated through an experimental determination of the electronic structure of both occupied and unoccupied adsorbate states in an atom specific way using x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) together with density functional theory calculations (DFT).²Footnote 2 @ It has been shown that the catalytic activity of different transition metals as catalysts for ammonia synthesis is given by the strength of the nitrogen-surface bond.³Footnote 3 @ We will show that XES, XAS and DFT studies of atomic nitrogen can probe details of the metal d induced adsorbate electronic structure that can be linked to the chemisorption bond strength. ¹FootnoteText¹ @footnote 1 @ B. Hammer and J. K. Nørskov, Nature 376, 238 (1995). ²Footnote 2 @ A. Nilsson and L. G. M. Pettersson, Surf. Sci. Repts. 55, 49 (2004). ³Footnote 3 @ A. Logadottir, T. H. Rod, J. K. Nørskov, B. Hammer, S. Dahl and C. J. H. Jacobsen, J. Catal. 224, 206 (2001).

3:40pm SS1-MoA6 Microcanonical Transition State Theory: Closing the "Nonequilibrium Gap" Between Surface Science, Catalysis, and Electronic Structure Theory, I. Harrison, University of Virginia

Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this "nonequilibrium gap" for several activated dissociative chemisorption reactions [e.g., CH₄ on Ni(100), Pt(111), and Ir(111); SiH₄ on Si(100); H₂ on Cu(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces.

4:00pm SS1-MoA7 First Principles Study of Factors Controlling the Rate of Ammonia Decomposition on Ni and Pd Surfaces, S. Stolbov, T.S. Rahman, Kansas State University

Using the plane wave pseudopotential method within the density functional theory with the generalized gradient approximation for exchange and correlation potential, we have calculated adsorption energies (E_{ad}), diffusion barriers and the first dissociation barriers (E₁) for NH₃ on Ni(111), Pd(111), Ni(211), and Pd(211). While the top site is found

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to be preferred for NH₃ adsorption on both Ni(111) and Pd(111), the calculated diffusion barrier is substantially higher for Pd(111) than for Ni(111). We also find that during the first dissociation step (NH₃ => NH₂ +H) on both surfaces NH₂ moves from the top site to the nearest hollow site, while on the stepped surface (211) it moves from the initial top site to the step edge to the bridge site in the same step chain. H is found to occupy the hollow sites for all four surfaces. For the reaction on Ni(111), E₁ is found to be 0.23 eV higher than E_{ad}, while at the step of Ni(211), E₁ and E_{ad} are almost equal. This suggests that the molecule would rather desorb than dissociate on Ni(111), and dissociate on the stepped surface. On the other hand in the case of Pd surfaces, we find that the dissociation barrier is much higher than E_{ad}, even for the stepped surface. This may explain why ammonia decomposition rate on Pd is much lower than that on Ni.

4:20pm SS1-MoA8 Water Chemistry on Cu(110): from Ultra High Vacuum to Ambient Conditions, K. Andersson, Stanford University / Stockholm University, Sweden; *H. Bluhm, G. Ketteler*, Lawrence Berkeley National Laboratory; *H. Ogasawara, T. Schiros*, Stanford Synchrotron Radiation Laboratory; *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory; *A. Nilsson*, Stanford Synchrotron Radiation Laboratory

Probing the coverage and chemical speciation of molecules at surfaces are of fundamental interest in the fields of heterogeneous catalysis and molecular environmental science. We present in-situ studies of water adsorption on Cu(110) at pressures up to 1 Torr in the temperature range 270 - 470 K using synchrotron-based photoelectron spectroscopy. Partial coverages of atomic O, OH, and H@sub 2@O are reported under various conditions. We compare our results to those obtained under ultra high vacuum conditions where we have found a water dissociation onset at about 160 K with an activation barrier of 0.53-0.56 eV.@footnote 1@ @FootnoteText@ @footnote 1@ K. Andersson, A. Gómez, C. Glover, D. Nordlund, H. Öström, T. Schiros, O. Takahashi, H. Ogasawara, L.G.M. Pettersson, A. Nilsson, Surf. Sci. Lett., in press (2005).

4:40pm SS1-MoA9 Hydrogen Interactions with Quasicrystalline Aln-; Pd- & n-; Mn Surfaces, C.J. Jenks, T.A. Lograsso, Ames Laboratory, Iowa State University; *J. Whaley, R. Bastasz*, Sandia National Laboratories

The interaction of molecular and atomic deuterium with the fivefold surface of icosahedral (i-) Aln-Pdn-Mn using angular-resolved low-energy ion scattering under ultrahigh vacuum conditions will be discussed. i-Aln-Pdn-Mn is known to form a clean laterally-bulk-terminated surface after sputtering and annealing in excess of 800 K. Despite no two layers within a this material being identical, certain types of planes are favored, namely those that are Al-rich (> 77 atomic percent). The density of Al atoms on the clean surface of fivefold i-Aln-Pdn-Mn is about that of Al(111) and thus we compare our results to studies of molecular and atomic hydrogen on Al(111). We are able to confirm, using ion scattering of 2 keV neon ions and direct recoil measurements, previous thermal desorption studies that indicated that molecular deuterium does not dissociate on this surface. Molecular deuterium, likewise, does not dissociate on Al(111). Atomic hydrogen, however, we find readily adsorbs on both surfaces. On fivefold i-Aln-Pdn-Mn we find that atomic deuterium adsorbs on top of the surface and that it strongly attenuates the signals for Al, Pd and Mn along particular azimuthal directions. Based on this information we will discuss the deuterium adsorption geometry on i-Aln-Pdn-Mn and compare the results to those for Al(111). This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences under Contracts no. W-405-Eng-82 and DE-AC04-94AL85000.

5:00pm SS1-MoA10 Detection of Nitric Oxide using Gold Nanoparticle Catalysts on WO@sub3@ Chemiresistive Sensors, A.L. Martin, University of Maine; *J. Wang*, Bangor High School; *G. Bernhardt*, University of Maine; *M. Sander*, Inst. Materials Res. Eng., Singapore; *R.J. Lad, F.G. Amar, B.G. Frederick*, University of Maine

Detection of nitric oxide at parts-per-billion levels is important for environmental and medical applications. We have shown that NO can be detected on tungsten trioxide chemiresistive sensors if gold or silver nanoparticles are present. The sensitivity, dynamic range, and response time depend upon the metal coverage and particle size distribution. In the limit that NO to NO@sub2@ conversion and spillover/diffusion is fast compared to NO@sub2@ reaction, the mean field solution is consistent with the initial, linear dependence of sensor response on NO partial pressure. Changes in the gold nanoparticle particle size distribution were measured with high resolution SEM. We have modeled the adsorption and conversion of NO to NO@sub2@ on the metal catalyst, followed by spillover, diffusion and reaction of NO@sub2@ with oxygen vacancies on the WO@sub3@(001) surface using kinetic Monte Carlo simulations. The

spatial inhomogeneity results in a non-linear sensitivity curve, which is consistent with sensor response after aggregation.

Surface Science

Room 203 - Session SS2-MoA

Oxide Surfaces Structure and Reactivity

Moderator: M.A. Langell, University of Nebraska-Lincoln

2:00pm SS2-MoA1 Reconstructions of the Polar Oxide Surface MgO(111), S.E. Chamberlain, D.A. Human, X.F. Hu, H.C. Poon, D.K. Saldin, C.J. Hirschmugl, University of Wisconsin-Milwaukee

Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g., hydroxylated surface, 2.) surface faceting, 3.) metallization.@footnote 1@ MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures, and reconstruct when heated to higher temperatures,@footnote 2@ and thus represents an ideal system for detailed structural analysis. Detailed surface structures for the 1x1 and (@sr@3 x @sr@3)R30 ° reconstructions will be presented, which have recently been obtained with a novel, low-current LEED system. In good agreement with recent photoelectron diffraction and electronic structure calculations,@footnote 3@ the MgO(111)1x1 surface is mostly terminated with adsorbed OH groups mixed with a small percentage of O terminated patches with significant relaxation, and suggests that the hydroxylated surface is the compensation method of choice for MgO(111) 1x1. Results from the (@sr@3 x @sr@3)R30 ° reconstruction will be compared with several structures proposed in the literature.@footnote 2,4@ @FootnoteText@ @footnote 1@ C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)@footnote 2@ R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L. D. Marks, M. Gajdardziska-Josifovska, Phys. Rev. Lett. 81 (1998) 4891.@footnote 3@ V. K. Lazarov, R. Plass, H-C. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, and M. Gajdardziska-Josifovska Phys. Rev. B 71, 115434 (2005)@footnote 4@ Subramanian A, Marks LD, Warschkow O, Ellis DE, Phys. Rev. Lett. 92 (2004)200411.

2:20pm SS2-MoA2 Effects of CH@sub 3@OH, H@sub 2@O and O@sub 2@ on Ultrathin Ordered Alumina Films under Non-UHV conditions: Hydrogen Bonding and Pressure Gaps, M. Jain, F. Qin, M. Magtoto, J. Kelber, University of North Texas

STM, AES and LEED have been used to probe the reactivities of ~ 7.5 Å thick, ordered Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al(110) and Ni@sub 3@Al(111) substrates for CH@sub 3@OH, H@sub 2@O and O@sub 2@ at intermediate pressures (10@super -8@ Torr - 10@super -1@ Torr) at room temperature. Results for H@sub 2@O show that at pressures above 10@super -4@ Torr, 300 K a surface reconstruction is initiated at defect sites which gradually leads to complete loss of long range order without formation of a UHV-stable hydroxide.@footnote 1@ The effect is pressure, rather than exposure-dependent, indicating a cooperative effect. Similar exposures to CH@sub 3@OH at > 10@super -4@ Torr, 300 K also induce a reorganization of the oxide film, though less severe than is observed for equivalent exposures of H@sub 2@O. STM constant current imaging at 2.0 V tip/sample bias of an Al₂O₃/Ni₃Al(111) film after a total CH₃OH exposure of 5.4 x 10⁵ L at 10@super -4@ Torr, 300 K, reveals disordering of the oxide surface. Imaging at 0.1 V, and LEED however, reveals that the oxide/substrate interface still retains long-range order. C coverage remains < 0.05 monolayers at all exposures. Exposures of Al@sub 2@O@sub 3@/Ni@sub 3@Al(111) and Al@sub 2@O@sub 3@/Ni@sub 3@Al(110) to pure O@sub 2@ at pressures > 10@super -4@ Torr, 300 K result in no change to the film observable by AES, LEED or STM. No effect is observed for any of these gases at pressures < 10@super -7@ Torr, even for exposure times > 6 hours. These data indicate that intermolecular hydrogen bonding is important for inducing cooperative reactions at oxide surfaces and intermediate pressures.The data will be discussed with regards to issues of oxide stability and metal particle sintering during catalytic reactions. @FootnoteText@@footnote 1@F. Qin, N.P. Magtoto, J.A. Kelber, Surf. Sci. 565 (2004) L277. This work was supported by the Robert Welch Foundation under grant B-1356.

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2:40pm **SS2-MoA3 Structural Characterisation and Reactivity of V@sub2@O@sub3@(0001) Thin Films**, *S. Guimond, M.A. Haija, A. Uhl, H. Kuhlbeck, H.J. Freund*, Fritz Haber Institute of the Max Planck Society, Germany

Vanadium oxides are used as catalysts for several oxidation reactions, including the selective oxidation of hydrocarbons and the oxidative dehydrogenation of alkanes to olefins. In spite of their importance, many questions about the molecular structure and the reaction mechanisms at their surfaces remain unanswered. For instance, a range of vanadium oxidation states exists (from 2+ to 5+) and it is often argued that lower oxidation states like V@sub2@O@sub3@ could take part in some of the reactions taking place at the surface of the V@sub2@O@sub5@-based catalysts. In the present work, we prepared well ordered V@sub2@O@sub3@(0001) thin films and studied their interaction with different molecules. The films were grown on Au(111) by evaporation of vanadium in a partial pressure of oxygen. Under typical UHV conditions, the films are terminated by vanadyl groups which are not part of the V@sub2@O@sub3@ bulk structure. As indicated by XPS and vibrational spectroscopy, the oxygen atoms contained in the V=O groups can be removed by electron irradiation, resulting in a surface terminated by metal atoms. This reduction process was followed with STM. The chemical activity of the two surfaces with respect to the adsorption of O@sub2@, H@sub2@O, CO@sub2@ and propane was investigated with XPS, IRAS and TDS. While the surface terminated by vanadyl groups was found to be chemically not very active, a rather high activity was observed for the V-terminated surface: O@sub2@ adsorption re-establishes the V=O groups via a charged precursor at low temperature, similar to the case of oxygen on Cr@sub2@O@sub3@(0001). After thermal desorption of an adsorbed CO@sub2@ layer, the surface is partially re-oxidized, meaning that part of the CO@sub2@ oxygen remains on the surface and forms vanadyl groups. Water dissociates on the surface, forming a layer of hydroxyl groups which is stable up to 500 K. Propane is partially transformed into propene, possibly via an oxygen-containing intermediate.

3:00pm **SS2-MoA4 The Multiple Roles of Oxygen in Organic Photo-oxidation on TiO₂: Insights from Studies on a Model Photocatalyst Surface**, *M.A. Henderson*, Pacific Northwest National Laboratory; *J.M. White, M.D. Robbins*, University of Texas at Austin; *H. Uetsuka*, Kanagawa Academy of Science and Technology, Japan; *H. Onishi*, Kobe University, Japan

The primary role that molecular oxygen has been viewed to play in organic photo-oxidation processes on high surface area TiO@sub 2@ photocatalysts has traditionally been restricted to that of an electron scavenger. However, some groups have proposed more direct involvement of O@sub 2@ in reactions with organics. Typical photocatalytic studies employ high surface area powders which are often difficult to characterize on the molecular scale. Results presented in this talk on a model TiO@sub 2@ photocatalyst, rutile TiO@sub 2@(110), provide more detailed information on the roles of O@sub 2@ and show that O@sub 2@ not only acts as an electron scavenger but also: is involved in thermal reactions with organics and OH groups, blocks organic adsorption sites, and competes with adsorbed organics for photo-generated holes. Results on the photo-oxidation of trimethyl acetate, isobutene and acetone will be used to illustrate these functions of O@sub 2@ during photocatalysis on TiO@sub 2@. Additionally, it will be shown that the function of oxygen oscillates through these different roles as a typical C@sub n@ hydrocarbon is oxidized to completion (i.e., to CO@sub 2@ and water) by sequential removal of C@sub 1@ units.

3:20pm **SS2-MoA5 Iron Oxide Thin Films as Supports for Model Catalytic Systems**, *S. Shaikhutdinov*, Fritz-Haber Institute, Germany

Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. A detailed understanding of the surface structure of the oxide films is a crucial prerequisite. It has been previously shown that well-ordered FeO(111), Fe₃O₄(111) and alpha-Fe₂O₃(0001) films can be prepared on a Pt(111) substrate in a controllable manner. In this presentation, we report on the determination of the surface structure of these iron oxide films using scanning tunneling microscopy, temperature programmed desorption and vibrational spectroscopy of CO as a probe molecule. In particular, we have found that the Fe₃O₄(111) surface is terminated by 1/2 monolayer (ML) of iron, with an outermost 1/4 ML consisting of octahedral Fe²⁺ cations situated above a 1/4 ML of tetrahedral Fe³⁺ ions. The most strongly bound CO, which desorbs at 230 K, is assigned to adsorption to Fe³⁺ cations present at the step edges, whose geometry is predicted on the basis of coordinative unsaturation and

excess surface charge concepts. For the alpha-Fe₂O₃(0001) surface, experimental and theoretical evidence is presented which shows that the hematite may be terminated with ferryl (Fe=O) groups, which has never been considered for iron oxide surfaces. In addition, the structure and adsorption properties of metals (Pd, Au) deposited on these films are studied. For example, CO is found to react with lattice oxygen of Fe₃O₄ at the Pd/oxide periphery. Oxygen adsorption at elevated temperatures resulted in structural changes of the system. The results for the model catalytic systems supported on the iron oxides are compared with data previously obtained for other (non-reducible) oxide films.

3:40pm **SS2-MoA6 Role of Dichlorocarbene in the Surface Chemistry of Halomethanes on Fe@sub 3@O@sub 4@(111)-(2X2) ; a Comparative Thermal Desorption Study**, *Y. Le, G.G. Totir, G.W. Flynn, R.M. Osgood*, Columbia University

Iron-oxide surface chemistry plays an important role in understanding chemical routes for the environmental degradation of chlorinated halocarbons. An earlier study had shown the importance of dichlorocarbene in controlling the thermal reaction products for CCl@sub 4@ chemisorbed on magnetite-terminated hematite surfaces. In this talk, we report on an investigation of the surface chemistry of CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on a UHV-prepared Fe@sub 3@O@sub 4@(111)-(2X2) selvedge of single-crystal @alpha@-Fe@sub 2@O@sub 3@ (0001). Our experiments use UHV, temperature programmed reaction and desorption (TPR/D) measurements of dosed surfaces, along with LEED and Auger probes. The TPR/D spectra show that dissociative formation of dichlorocarbene, followed by its reaction with lattice oxygen and other adsorbed surface species, is central to the surface chemistry of halocarbons in general, and of halomethanes in particular on the (2X2) reconstructed surface of hematite. The specific branching ratios of the various desorbed products including metal-halides are compared for adsorbed CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on the (2X2) surface. Our experiments show clearly the importance of CCl@sub 2@ intermediates in these surface reactions.

4:00pm **SS2-MoA7 Methyl Radical Chemistry on Clean and UO@sub3@-Covered Single Crystal Hematite Surfaces**, *L. Liu*, Columbia University; *P.C. Stair*, Northwestern University

The partial oxidation of methane over oxide catalysts is controlled by the surface reaction of methyl radicals. Methyl radical chemistry was studied on two model surfaces in UHV: Clean, (0001) orientation single crystal hematite and UO@sub 3@ supported on a crystalline hematite thin film. Temperature Programmed Desorption (TPD) showed that methyl radicals adsorb on the Fe@sub 3@O@sub 4@ (111)-terminated hematite (0001) surface at 300 K and desorb intact at higher temperatures. At saturation coverage, the XPS C(1s) line position is consistent with methoxide ions on the surface, and the carbon-surface bond energy determined by threshold TPD analysis is similar to the C-O bond energy of surface methoxide ions. In contrast, methyl radicals produce only very small desorption features on the biphasic-terminated hematite (0001) surface. The coverage of adsorbed methyl was obtained by quantification of the TPD data. Saturation coverage was 1x10@sup 14@/cm@sup 2@ on the Fe@sub 3@O@sub 4@ (111)-terminated surface but only 3.7x10@sup 12@/cm@sup 2@ on the biphasic-terminated surface, consistent with adsorption on regular surface sites and defect sites, respectively. Since the two surfaces both contain Fe@sup 2+@, Fe@sup 3+@, and O the differences in methyl radical adsorption must be due to differences in surface structure. Based on an analysis of the structures reported in the literature it is proposed that methyl radicals adsorb on surface oxygen atoms with a dangling bond perpendicular to the surface plane on the Fe@sub 3@O@sub 4@ (111)-terminated surface. On the hematite-supported UO@sub 3@ surface, partial oxidation products, such as methanol, formaldehyde, and CO were identified by TPD. XPS quantification indicates that UO@sub 3@ forms a monolayer structure on the hematite support. The increased reducibility of UO@sub 3@ compared to hematite is responsible for the change in surface chemistry. A surface methoxide ion is the proposed reaction intermediate.

4:20pm **SS2-MoA8 Characterization of the Co@sub 3@O@sub 4@(111) Single Crystal Surface**, *E.M. Marsh, M.A. Langell*, University of Nebraska-Lincoln

The (111) face of the Co@sub 3@O@sub 4@ single crystal has been characterized using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED) to establish the cleanliness, composition, and order of the (111) surface. The vibrational modes of the Co@sub 3@O@sub 4@(111) face were then investigated by high-resolution electron energy loss spectroscopy (HREELS)

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and the Fuchs-Kliwer phonon spectrum was obtained with an incident electron energy of 3.77 eV. Data taken on the (111) surface has been compared to previously reported values taken from the (110) surface of the Co_3O_4 single crystal. HREELS was also used to study the vibrational modes of H_2O as an adsorbate on the surface to test the accuracy of the log-deconvolution algorithm in removing the multiple scattering modes of the phonon spectrum.

4:40pm **SS2-MoA9 The Interaction of Carbonyls with Oxide Surfaces: The Adsorption of Formaldehyde on $\text{CeO}_3(111)$** , *J. Zhou, D.R. Mullins*, Oak Ridge National Laboratory

Formaldehyde, CH_2O , chemisorbs on both oxidized and reduced cerium oxide surfaces. Near-edge X-ray Absorption Fine Structure (NEXAFS) and synchrotron-excited Soft X-ray Photoelectron Spectroscopy (SXPS) indicate that chemisorption occurs through the formation of a dioxymethylene, CH_2O_2 , intermediate. On the fully oxidized surface this intermediate is weakly bound and results in molecular formaldehyde desorption between 200 K and 300 K. On a reduced cerium oxide surface the intermediate is more strongly adsorbed and desorbs as formaldehyde near 460 K. Some of the dioxymethylene disproportionates producing formate and methoxy intermediates above 450 K. These intermediates dissociate to form H_2O and CO products above 550 K. At large formaldehyde exposures polymerization occurs on both the oxidized and reduced ceria surfaces. The polymer decomposes to produce formaldehyde between 300 K and 400 K. The adsorption of formaldehyde, which occurs through the conversion of the carbonyl to carbondioxy on the oxide surface, is contrasted with the adsorption of methanol in which the hydroxyl bond is broken and methoxy is formed on the ceria. The methoxy group is more stable than dioxymethylene on the ceria surface and leads to decomposition products above 560 K rather than the recombinative desorption of methanol. 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.

5:00pm **SS2-MoA10 Structure and Reactivity of the Positively and Negatively Poled Surfaces of $\text{LiNbO}_3(0001)$** , *M. Li, D. Liao, E.I. Altman*, Yale University

The effect of ferroelectric poling direction on the structure and reactivity of the $\text{LiNbO}_3(0001)$ surface was studied using reflection high energy and low energy electron diffraction, x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy, and temperature programmed desorption (TPD). The surfaces were prepared by annealing at 1175 K in air at atmospheric pressure and then cleaned by exposure to oxygen plasmas in UHV. Following this procedure, both the positive and negative surfaces gave (1×1) diffraction patterns. No evidence of reconstructions was observed suggesting that both surfaces are bulk terminated with the negatively poled surface exposing Li ions and the positive surface Nb ions, in contrast to prior work that suggested an oxygen termination for both surfaces that would require a reconstruction to maintain the proper stoichiometry. Photoelectron spectra also showed little difference between the positive and negative surfaces with both showing Nb only in the 5+ oxidation state, and valence level spectra with nearly identical emission due to O 2p derived states and no emission in the bandgap due to reduction. These results are also in contrast to a prior study that suggested reduction of the Nb ions near the negatively poled surface. Differences in reactivity of the two surfaces towards CO_2 , water, and 2-propanol is being characterized using TPD along with XPS and UPS.

Monday Afternoon Poster Sessions, October 31, 2005

Surface Science

Room Exhibit Hall C&D - Session SS-MoP

Surface Science Poster Session

SS-MoP2 Probing the Vibrational State-Resolved Gas-Surface Dynamics of CH₄ on Ni(111). V. Campbell, Tufts University

We describe an experimental approach that yields vibrational-state-resolved reaction probabilities for polyatomic molecules without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study and its vibrational energy transfer dynamics in a supersonic expansion. In the case of methane, non-equilibrium cooling of vibrational states within polyads leads to the population of a single vibrationally excited state under easily obtained expansion conditions, even though several excited vibrational states would contain significant population under the nominal thermal conditions of the nozzle source. We apply this approach to extract state-resolved reaction probabilities for methane in the CH₄ vibrational fundamental and incident on clean Ni(111) surface. State-resolved reaction probabilities obtained in this way are free from the vibrational-state averaging that clouds interpretation of beam-surface reactivity measurements and permit a more direct test of theoretical models of gas-surface reactivity.

SS-MoP3 Alkylidene Functionalization of Molybdenum Carbide Surfaces: Thermal Stability and Chemical Reactivity. H. Oudghiri-Hassani, M. Sijaj, I. Temprano, C. Maltais, P.H. McBreen, Université Laval, Canada

Metal carbides possess a blend of metallic and ceramic properties and are amenable to unique surface modification procedures. In particular, molybdenum carbide surfaces may be functionalized using alkylidene groups. Such groups involve a double bond between the organic component and a single molybdenum atom at the surface, as distinct from bridge-bonded structures. We have previously shown that surface alkylidenes on molybdenum carbide display anomalously high thermal stability. The origins of this thermal stability will be discussed on the basis of extensive synchrotron photoemission, RAIRS and isotope substitution desorption data. The combined data reveal a key role for excess surface carbon in stabilizing the alkylidene groups to temperatures as high as 900 K. Furthermore, it will be shown that the metathesis activity of the surface alkylidene initiating sites may be used to perform add-on functionalization using a variety of olefins and substituted olefins.

SS-MoP4 Sulfur-CO Interactions on Cu(100) Films through Surface Resistivity and Infrared Reflectance Measurements. C. Liu, R.G. Tobin, Tufts University

Interactions between dissimilar adsorbates on Cu(100) thin films have been investigated experimentally through their effects on electrical transport in the metal. We report measurements of surface resistivity induced by CO on 50 nm-thick epitaxial Cu(100) films preadsorbed with different amounts of sulfur, together with temperature-programmed desorption (TPD) and infrared reflectance measurements. Adsorbate-induced surface resistivity arises from the scattering of conduction electrons in the metal from the impurity potential created by the adsorbate. Previous experiments have shown that the scattering cross section of sulfur decreases with increasing coverage, indicating a strong sulfur-sulfur interaction. In the present work, sulfur-CO interactions are explored by measuring the slope of the resistivity vs. CO coverage curve as a function of sulfur precoverage. Effects of sulfur on CO's scattering cross section are revealed as changes in the slope. Sulfur-induced changes in CO adsorption are also monitored with infrared vibrational spectroscopy and TPD. @FootnoteText@ @footnote 1@R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-MoP5 Adsorption Geometries of Prochiral Molecules on Pt(111): Heterogeneous Enantioselective Hydrogenation. M.A. Laliberté, A. Rouffignat, I. Temprano, S. Lavoie, P.H. McBreen, Université Laval, Canada HREELS and RAIRS were used to study the adsorption of carbonyls and dicarbonyls on Pt(111) with the goal of better understanding the Orito reaction. The Orito reaction describes the enantioselective hydrogenation of the keto-function of alpha-ketoesters on chiral-modified platinum particles. Measurements were performed on acetone, ethyl formate, biacetyl, methyl pyruvate and ethyl pyruvate adsorbed on clean Pt(111), and coadsorbed with toluene, benzene, naphthalene, methyl naphthylene, cyclohexane and naphthylethylamine. Very strong

coadsorption interactions resulting in complete modification of the adsorption geometries of the carbonyl molecules were observed for several of these systems. The results aid in mapping out the range of adsorption geometries available to dicarbonyl substrates in the Orito reaction. The results will be discussed in the context of a proposed new mechanism for the enantioselective reaction.

SS-MoP6 "Hot Electrons" at Organic-Metal Interface: Photodissociation of Phenol on Ag(111). S. Ryu, J. Chang, S.K. Kim, Seoul National University, Korea

Photodissociation of many organic adsorbates on metal surfaces has been attributed to photoexcited "hot electrons". To address this issue, we have explored the interfacial electronic structure of phenol adsorbed on Ag(111) using time-resolved two-photon photoemission spectroscopy. The photoinduced anion state of phenol was found at 3.1 eV above the Fermi level at one monolayer coverage. The binding energy of this state remained constant at around 0.7 ~ 0.8 eV for all coverages. Polarization dependence of the photoelectron signal revealed mechanistic details for each excitation step. The lifetime of the anion state was found to increase from 33 to 60 fs, indicating its lesser coupling to the bulk as the coverage increased from 1 to 9 ML. These findings demonstrate the role of hot electrons in photodissociation of adsorbates.

SS-MoP7 Interaction of Sulphur-Containing Anions with Copper Single Crystal Electrodes. J. Hommrich, S. Hümann, P. Broekmann, K. Wandelt, A. Spänig, University of Bonn, Germany

Processes at metal/electrolyte interfaces are a promising route to modify and structure surfaces on the nanometer scale. This, because processes at metal/electrolyte interfaces may be easier to control than those in vacuum, and are probably more economic. In this contribution we summarize results for sulphur-containing anion adsorption from solution on single crystal copper electrodes as obtained with in-situ ElectroChemical Scanning Tunneling Microscopy (ECSTM) and Fourier-Transform Infrared Spectroscopy (FTIRS) in combination with ex-situ surface analytical methods like AES, LEED, XPS, ISS etc. Hetero-atoms like, for instance, sulphur are often the anchors through which organic molecules are bound to surfaces. In particular, results will be presented and discussed for the most basic anionic groups, namely SO₄²⁻ and S²⁻, as well as derivatives thereof like sulfonate and thiocyanate anions on Cu(111) and Cu(100) electrodes. Special emphasis will be placed on the adsorbate structure and dynamics, on structural phase transitions, adsorption induced surface reconstruction as well as chemical stability as a function of electrode potential.

SS-MoP8 Electrochemical Formation of a Semiconducting Metal Oxide observed by In Situ Tunneling Spectroscopy. I. Diez-Perez, A. Guell, University of Barcelona, Spain; P. Gorostiza, University of California, Berkeley; F. Sanz, University of Barcelona, Spain

Obtaining tunneling spectroscopic data in electrolytic solutions is fundamental to understand electrode reactivity. Electrochemical scanning tunneling spectroscopy (ECTS) represents a powerful method for the in situ elucidation of the electronic structure on solid-electrolyte interfaces. Its experimental realization has been reported only in a few instances with some limitations. We present tunneling spectra of an Fe electrode immersed in a borate buffer electrolyte while it is reversibly oxidized to different potentials within the three oxidation ranges: Fe(0), Fe(II) and Fe(III). Complete series of ECTS spectra within the entire Fe passivation range allow us the representation of oxide surface conductograms by plotting the e- energy level on the Y-axis (tip potential), the electrode oxidation state on the X-axis (sample potential) and surface conductance represented by the Z gray scale. Our spectra span up to 2.2V using high tip potential scan rates (up to 15V/s). We have developed a new method to prepare and isolate Pt/Ir tips specially for in situ STS applications. Under conditions where the passive film is chemically stable in the working buffer, we found that the different redox transitions at the iron surface result from the availability of free charge carriers controlled by electron energy barriers at the oxide/solution interface. The passivity of iron results from the build-up of an energy barrier in n-Fe(III) and the absence of states available for charge exchange within almost 1.5eV below the CB edge. Increasing the sample potential in the passive plateau results mostly in increasing the band bending inside the oxide and decreasing the electron concentration. @FootnoteText@ @footnote 1@E.Tomita, N. Matsuda, K. Itaya, J. Vac. Sci. Technol., A8(1)534(1990). @footnote 2@I. Diez-

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Perez, P. Gorostiza, F. Sanz. *J. Electrochem. Soc.*, 150: B348 (2003). @footnote 3 @ A. G. Guell, I. Diez-Perez, P. Gorostiza, F. Sanz, *Anal. Chem.*, 76, 5218. (2004).

SS-MoP9 Interaction of Water Vapor with Clean and Contaminated Ru Surfaces, B.V. Yakshinskiy, N.S. Faradzhev, T. Graber, T.E. Madey, Rutgers, The State University of New Jersey

We compare the interaction of water vapor (H_{2O} and D_{2O}) with two important surfaces of hcp Ru: the atomically-rough (10-10) and the smooth close-packed (0001) surfaces. Several methods, including temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and low energy ion scattering (LEIS) were used to study adsorption/desorption processes of water on the clean surfaces, as well as on carbon-dosed, oxygen-dosed and air-exposed surfaces. Both H_{2O} and D_{2O} undergo partial dissociation upon adsorption/desorption on Ru(10-10), which is in contrast to Ru(0001), where there is a striking isotope effect: D_{2O} is adsorbed molecularly, without dissociation, whereas H_{2O} dissociates partially. The data show non-wetting behavior of water on the air-exposed or the carbon-covered surfaces, but water becomes more strongly bonded to an oxygen-dosed substrate. We also report on the electron-induced dissociation and the electron-stimulated desorption (ESD) of water adsorbed on these surfaces at low temperature. The data provide insights into recent controversy concerning the interaction of water with Ru surfaces.

SS-MoP10 XPS and Sulfur K-edge NEXAFS Characterization of Isotope Effect for Coadsorption Systems (H_{2O} or D_{2O})/L-Cysteine/Cu(100), S. Yagi, D. Tomihara, T. Nomoto, Nagoya University, Japan; G. Kutluk, JST, Japan; M. Taniguchi, Hiroshima University, Japan; K. Soda, Nagoya University, Japan

Adsorption structure and chemical property of a sulfur-containing amino acid molecule of L-Cysteine on transition metal surface has been interested in a bio-compatibility, a bio-catalysis and a bio-materials fields. XPS (X-ray Photoelectron Spectroscopy) and NEXAFS (Near edge X-ray Absorption Fine Structure) techniques have established themselves as a powerful tool to characterize both a local molecular adsorption structure and a chemical condition of the adsorbates at adsorption sites. In the present study, we have paid attention to the isotope effect for coadsorption systems (H_{2O} or D_{2O})/L-Cysteine/Cu(100) studied by coupling of (S_{2p} , C_{1s} , O_{1s} and N_{1s}) XPS and sulfur K-edge NEXAFS measurements. There are some dominant differences in the experimental results of XPS and NEXAFS spectra for coadsorption systems of (H_{2O} or D_{2O})/L-Cysteine/Cu(100).

SS-MoP11 Covalent Attachment of Pt-Dendrimer Encapsulated Nanoparticles to 11-Mercaptoundecanoic Acid Thin Films, T.J. Black, K.A. Perrine, Y. Gu, H.J. Ploehn, D.A. Chen, University of South Carolina

Polyamidoamine dendrimers represent a diverse tool for chemical and biological research due to their functionality and highly tunable properties. The work presented here takes advantage of the dendrimer's ability to act as a nanoscale template for controlling the size distribution of metal particles formed in solution. Specifically, amine-terminated, generation 4 polyamidoamine dendrimers ($G4-NH_{2}$) are treated with $K_{2}PtCl_{6}$ in a metal:dendrimer ratio of 40:1 to coordinate approximately 40 Pt^{2+} ions inside each dendrimer. Subsequent reduction with $NaBH_{4}$ is believed to form metallic Pt particles ~2 nm in diameter according to transmission electron microscopy studies. We have optimized a procedure that covalently links the dendrimer encapsulated nanoparticles onto a self-assembled monolayer of 11-mercaptoundecanoic acid (MUA) on Au(111) surfaces; this robust dendrimer film allows for various mechanical and chemical treatments that would not otherwise be possible. After the MUA monolayer is exposed to EDC (1-[3-(diethylamino)propyl]-3-ethylcarbodiimide hydrochloride) and an NHS (hydroxysuccinic acid)catalyst followed by treatment with the dendrimer solution, infrared reflection absorption spectroscopy (IRAS) experiments suggest that amide bonds are formed between the SAMs and the dendrimer by the disappearance of the carboxylic acid mode at 1722 cm^{-1} from the MUA accompanied by the appearance of amide modes at 1670 cm^{-1} and 1556 cm^{-1} . X-ray photoelectron spectroscopy also confirmed the presence of Pt- $G4NH_{2}$ on the SAMs since nitrogen and platinum signals were detected. The next step of this project will be to remove the dendrimer templates and SAM from the Au(111) surface by oxidation-reduction cycles, leaving behind the Pt nanoparticles. The ultimate goal of this work is to study the surface chemistry of the supported, well-characterized Pt particles in model catalytic reactions, such as CO oxidation.

SS-MoP12 Adsorption and Hydrogenation of 1,3-butadiene on Pd(111) and Pd-Sn/Pd(111) Surface Alloys, Chr. Breinlich, J. Haubrich, C. Becker, K. Wandelt, University of Bonn, Germany

The selective hydrogenation of dienes into mono-olefines is an important industrial reaction. Industrial processes are usually carried out with supported catalysts containing transition metals such as palladium or platinum. Palladium shows a high activity and selectivity for these reactions. Therefore we have studied the adsorption and hydrogenation of 1,3-butadiene on Pd(111) and Sn-modified Pd(111) surfaces. The Pd-Sn surface alloys were produced by annealing of tin layers of various thicknesses. Depending on the amount of deposited tin this procedure actually resulted in ordered surface alloys of ($3x3$) R_{30}° or $p(2 \times 2)$ superstructure, which were characterized by LEED, AES and UPS. The adsorption and reaction of 1,3-butadiene was investigated by TPD. After 1,3-butadiene adsorption at 55 K the desorption of the multilayer was found near 120 K on all surfaces. Further heating lead to the complete dehydrogenation of the butadiene on the Pd(111) surface. On the surface alloys only a part of the butadiene dehydrogenates while the rest desorbs at 200 - 230 K. By preadsorbing either hydrogen or deuterium the 1,3-butadiene can be partially hydrogenated to butene on the surface alloys. The partial hydrogenation is highly selective since no desorption of butane has been found. The branching ratio of desorption vs. hydrogenation on the surface alloys is clearly a function of the amount of tin, which was deposited and, hence, the surface stoichiometry. HREELS investigations reveal the adsorption modes of 1,3-butadiene and butene on these surfaces.

SS-MoP13 Oxygen-induced Faceting of NiAl(111), E. Loginova, W. Chen, N.M. Jisrawi, T.E. Madey, Rutgers University

We report the adsorption of oxygen and oxygen-induced faceting of NiAl(111), as studied by means of LEED, AES and high-resolution soft XPS (HRSXPS, using synchrotron radiation at NSLS). The atomically rough NiAl(111) surface remains planar at room temperature when exposed to oxygen. However, the surface changes its morphology and becomes faceted upon annealing at 1100K and higher; nucleation and growth of facets are studied. The adsorption and reaction of oxygen are characterized by HRSXPS measurements of Al 2p and Ni 3p core levels for the faceted and planar surfaces. The data indicate that a well-ordered thin aluminum oxide film can be formed on the faceted NiAl surface. Our work is motivated by the possibility that self-organized alumina thin-film-covered NiAl facets might be used as templates for uniform growth of metallic nanostructures with controlled size and spacing. The Al $_{2O_{3}}$ /NiAl(111) system is a good model material for studying catalytic reactions over Al $_{2O_{3}}$ -supported metal catalysts.

SS-MoP14 Adsorption of Sulfur Dioxide on Zircaloy-4, N. Stojilovic, R.D. Ramsier, The University of Akron

The adsorption of sulfur dioxide on Zircaloy-4 surfaces is investigated using Auger electron spectroscopy. We find that both surface oxidation and saturation with sulfur and oxygen occur at low coverages at 300 K. Heating above 800 K results in oxygen dissolution into the bulk whereas sulfur stays in the near surface region. We examine effects of this residual sulfur on subsequent sulfur dioxide and oxygen adsorption. In both cases the adsorbates oxidize the sulfur-contaminated surface. Sulfur dioxide exposures at 300, 600 and 900 K all result in similar amounts of surface sulfur, indicating similar sticking coefficients in this temperature range. However, 900 K adsorption does not result in a shift of the Zr(MNN) feature that would signify surface oxidation. Thus this system can either adsorb or absorb oxygen from sulfur dioxide depending on the temperature, and the sulfur remains trapped near the surface without poisoning it with respect to subsequent oxidation.

SS-MoP15 Surface and Bulk Electronic Structures of Heusler-type Fe@sub 2@Al, M. Miyazaki, K. Soda, S. Yagi, M. Kato, T. Takeuchi, Nagoya University, Japan; U. Mizutani, Toyota Physical and Chemical Research Institute, Japan; Y. Nishino, Nagoya Institute of Technology, Japan

Surface and bulk electronic structures of Heusler-type Fe $_{2}$ Al have been studied by both surface- and bulk-sensitive photoelectron spectroscopy, in particular, for the valence band and V 2p core level regions, in order to elucidate the changes in the valence band electronic structures for the surface and bulk regions and to clarify the mechanisms of its unusual transport properties@footnote 1@ and of the large enhancement of its thermoelectric power on a small deviation in the chemical composition.@footnote 2@ The valence band spectrum reveals fairly large intensity at the Fermi level E_{F} for the surface-sensitive low photon energy excitation but considerably small E_{F} intensity

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for the bulk-sensitive high photon energy excitation. This intensity reduction implies that a pseudogap is formed around E_F in the bulk electronic structure, as predicted by band calculations.² The intensity between the binding energy of 0.4 eV and E_F is relatively increased for the large photoelectron takeoff angle (measured from the surface normal). These facts indicate that the pseudogap is destroyed in the surface layers. The V 2p core level spectrum shows a surface-derived satellite structure in the low binding energy side of the main bulk band. This suggests that the valence electron concentration around V may be large in the surface region in comparison to the bulk. We will discuss the surface and bulk electronic structures with use of a DV-X α local electronic structure calculation. ¹ Y. Nishino et al., Phys. Rev. B71, 094425 (2005). ² Y. Nishino, Materials Trans. 42, 902 (2001).

SS-MoP16 Growth and Oxidation of Ultrathin Films of Zirconium on the Au(111) Surface, T.J.Z. Stock, Queen's University, Canada; A.J. Slavin, Trent University, Canada

The growth and oxidation of ultrathin zirconium films (to 5 atomic layers) on the gold(111) surface in ultrahigh vacuum have been studied as a function of substrate temperature and oxygen pressure. The oxide films are of interest as a possible replacement for SiO₂ in the gate of field-effect transistors. The study has used Auger electron spectroscopy, electron energy-loss spectroscopy, low energy electron diffraction and work function measurements. The evolution of the chemical composition of the oxide layer has been followed using a high-stability quartz-crystal microbalance.¹ ² L. Bouzidi, S.S. Narine, K.G. Stefanov and A.J. Slavin; A high-stability quartz-crystal microbalance for investigations in surface science. Rev. Sci. Instrum. 74, 3039-3044 (2003).

SS-MoP17 Adsorption of Acetic Acid on Zn_xNi_{1-x}O, H.G. García Flores, University of Nebraska-Lincoln and Los Alamos National Laboratory; A. Starace, M.A. Langell, University of Nebraska-Lincoln

Zinc can be dissolved in rocksalt NiO to produce solid solutions of Zn_xNi_{1-x}O over an approximate composition range of 0 \leq x \leq 0.35. Both metals are formally M²⁺, typically the stable oxidation state in oxides, but the octahedral coordination site of the cations in the rocksalt structure is unusual for zinc, which is typically tetrahedral as is found in wurtzite ZnO. The unique chemical environment of the zinc-nickel oxide solid solution can potentially result in new and interesting surface reactivity. Solid solutions of the zinc-nickel oxide over the range of 0.05 \leq Zn \leq 0.35 were prepared by calcination at 1200 K and were characterized using powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). The Auger parameter for zinc in these homogeneous solid solutions increases indicating stronger ionic character. Acetic acid (CH₃COOH) was then used to examine the surface reactivity of the mixed-metal solid solution in a series of adsorption experiments that were carried out as a function of zinc concentration and surface pretreatment. At 250 K, the primary adsorbate observed is bidentate acetate and, once formed, the species is stable on the substrate to approximately 500 K.

SS-MoP18 Adsorption and Reaction of CO and CO₂ on Oxidized and Reduced SrTiO₃(100) Surfaces, L. Wang, Pacific Northwest National Laboratory; S. Azad, Rice University; M.H. Engelhard, Pacific Northwest National Laboratory

The adsorption and reaction of CO and CO₂ on oxidized and reduced SrTiO₃(100) surfaces have been studied using temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). XPS results indicate that the oxidized SrTiO₃(100) surfaces are nearly defect-free with predominantly Ti⁴⁺ ions whereas the sputter-reduced surfaces contain substantial amounts of defects. Both CO and CO₂ are found to adsorb weakly on the oxidized SrTiO₃(100) surfaces. The desorption activation energies of CO and CO₂ from the oxidized SrTiO₃(100) surfaces are 38 and 32 kJmol⁻¹, respectively, following adsorption at 110 K. On sputter-reduced surfaces, enhanced reactivity of CO and CO₂ is observed due to the presence of oxygen vacancy sites that are responsible for dissociative adsorption of these molecules. Our studies indicate that CO and CO₂ molecules exhibit relatively weaker binding to SrTiO₃(100) compared with TiO₂(110) and TiO₂(100) surfaces. These differences can be attributed primarily to the influence of the Sr cations on the electronic structure of the Ti cations in the mixed oxide of SrTiO₃.

SS-MoP19 Molecular Dynamics Study of the Aluminum/Alumina Interface Using an Efficient Charge-Transfer Potential, B.D. Devine, University of Florida; A.J.H. McCaughey, University of Pittsburgh; S.B. Sinnott, S.R. Phillpot, University of Florida

Many of the properties that make aluminum a desirable commercial material are attributable to it rapidly forming a passivating oxide layer. In studying the properties of such active metals, the nucleation of the oxide phase, its structural evolution, and the resulting interfacial effects must be considered. Mechanistic exploration of oxide formation is challenging at the atomistic level due to length and time scale limitations, and the complexity of simultaneously modeling a metal and its oxide. Here, the aluminum/alumina interface is investigated using classical molecular dynamics simulations. The empirical, charge-transfer Streitz-Mintmire¹ potential is coupled with an efficient direct pairwise summation of the Coulombic interactions.² The merits of the computational approach will be critically evaluated with the intent of applying the techniques to a large scale MD simulation of oxide formation and microstructure evolution. This work is supported by the National Science Foundation (grant no. DMR-0426870). ¹ F. Streitz, J. Phys. Rev. B 1994, 50, 996 ² Wolf et al., J. Chem. Phys. 1999, 110, 8254.

SS-MoP21 Investigation of sp² Carbon in Nanodiamond, J. Hu, J. Foord, University of Oxford, UK, United Kingdom

Diamond electrodes have wide application in electroanalysis, electrolysis, waste water treatment etc. due to superior properties, such as chemical inertness, high overvoltage, and resist to electrode fouling. The sp² carbon inclusion in microcrystalline and nanodiamond is believed to make a major contribution to the performance of diamond electrodes. We investigate this in the present paper. Microcrystalline and nanodiamond films are grown on Si (100) and polished Ti sheet with different methane concentrations by MWCV. The samples are characterized by Raman Spectroscopy, SEM, XPS, Voltammetry and conductivity. With increasing concentration of methane from 1% to 4%, the grain size decreases slightly and becomes more homogeneous. With further higher concentration of methane, the samples are nanocrystalline with typical grains of around 200 nm. XPS and EELS indicate that only a trace amount of sp² carbon is present on sample surface. About 1% percent of sp² carbon in microcrystalline diamond is etched away in electrochemical polarization at 2.2V in 1M HNO₃ solution, and more sp² carbon can be etched away for nanodiamond. This shows that most of the sp² carbon inclusions are present in grain boundaries instead of embedded into diamond grains or present as graphite grains at the electrode surface. Electrochemical etching protocols are examined, to minimize unwanted effect of sp² carbon on the performance of diamond electrode.

SS-MoP22 Imaging the Structure of Natural Organic Matter Adsorbed onto Carbonaceous Surfaces with Atomic Force Microscopy, J. Gorham, H. Fairbrother, Johns Hopkins University

Developing a microscopic understanding of the adsorbate layers formed by Natural Organic Matter (NOM) on carbonaceous surfaces is useful in developing more realistic models under environmental conditions. This information could also have important technological ramifications for water treatment strategies where NOM reduces the adsorptive capacity of activated carbons. In this study, the adsorption of NOM (obtained from the Great Dismal Swamp, VA) on Highly Ordered Pyrolytic Graphite (HOPG) has been studied at the liquid-solid interface using Atomic Force Microscopy (AFM). In these studies HOPG was used to model the extended graphene sheets that characterize the exposed surface of activated carbons. Under low pH conditions (pH 4.0), NOM particles were observed to cover the entire HOPG surface with a layer thickness of ~2 nm. Evidence of ordered adsorbate structures involving NOM were observed at low pH. As the pH of the NOM solution increased, the surface concentration of NOM decreased systematically; at pH 10, <10% of the HOPG was covered by adsorbed NOM. Particle size was also influenced by pH with the average size of adsorbed structures being greater at higher pH. The structure of adsorbed NOM was significantly modified by drying with "ring like" structures and larger NOM aggregates observed. Results will also be presented on the effect of ionic strength on the structure of the adsorbate layer.

SS-MoP23 Selective Reduction of MoO₃ Nanostructures on Au(111), D.S. Pinnaduwa, X. Deng, M.M. Biener, C.M. Friend, Harvard University

Well-ordered MoO₃ nanostructures on Au(111) have been prepared using iterative dosing of Mo(CO)₆ and NO₂. A

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c(4x2) unit cell is observed for these nanostructures in scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The presence of Mo⁶⁺ is confirmed by X-ray photoelectron spectroscopy (XPS). Selective reduction of MoO₃ nanostructures has been achieved by annealing at 650 K for varying times. Sheer planes are observed in STM due to the formation of Mo⁵⁺. Based on XPS data, ultimately, thermal reduction results in Mo⁶⁺ and Mo⁵⁺ at a 1:1 ratio on the Au surface. However, Mo⁴⁺ is absent in all thermal treatments, indicating the existence of a kinetic barrier for the reduction of either Mo⁶⁺/Mo⁵⁺ to Mo⁴⁺.

SS-MoP24 LEED and XPS Study of the Oxidation Process on Cu(111), K. Moritani, JAERI, Japan; *M. Okada*, Osaka University, Japan; *Y. Teraoka*, A. Yoshige, JAERI, 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. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes and the oxygen induced reconstruction on Cu(111) is far less clear. It is advantageous to control oxidation processes and structure in order to understand the chemical reactions and oxide formation processes on the nanoscale. In this work, we studied the oxidation of Cu(111) surface with a hyperthermal O₂ molecular beam (HOMB) and thermal O₂ gas using low energy electron diffraction (LEED) and 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 O₂ can be controlled by changing the O₂, He and/or Ar gas mixing ratios and the nozzle temperature. After the irradiation of a proper amount of HOMB or thermal O₂ gas, high-resolution XPS spectra were measured at ~300 K using SR and then LEED pattern was observed. We measured O-uptake curves, determined from the integration of O-1s XPS on the surface, after the HOMB irradiation or the exposure to the oxygen atmosphere. The oxidation with under 0.23 eV HOMB at room temperature saturated at 0.3 ML, when only (1x1) and diffused background LEED pattern was observed. The additional incident energy above 0.5 eV promoted the further oxidation above 0.3 ML and induced the reconstruction to c(8x8) phase where the O-1s peak sifted the low binding energy side. This reconstruction and peak shift were observed after thermal gas exposure at the higher temperature. We discuss possible models of oxidation process on the basis of the incident-energy and temperature dependence of the O-1s XPS spectra and LEED pattern.

SS-MoP26 Computational Study of the Deposition of Metal-Oxide Thin Films, J.M. McKillip, S.R. Phillpot, S.B. Sinnott, University of Florida

Thin film deposition of SrTiO₃ is currently a popular area of research due to its widespread use in electronic applications and the motivation to shrink electronic components. Pulsed laser deposition (PLD) is an effective deposition process yielding dense, homogeneous thin films. Here, classical molecular dynamics simulations are used to determine the mechanisms involved in PLD. The simulations show that collisions that occur between the incident particles and the substrate can induce chemical reactions. The simulations consider the deposition of SrO and TiO₂ molecules with a kinetic energy between .1 and 1 eV/atom on a (001) surface of SrTiO₃. The effects of impact energy, orientation of incident particles, and surface termination layer (SrO vs. TiO₂) are examined. The main surface phenomenon of interest is chemical changes that occur at the oxide surface due to the ablating particles. The simulation results are compared to experimental data, where available. This work is supported by the National Science Foundation (DMR-0426870).

SS-MoP29 Chain Structure of Surface Hydroxyl Groups on TiO₂(110) with Line Oxygen Vacancy Studied by in-situ Noncontact Atomic Force Microscopy (NC-AFM), Y. Namai, O. Matsuoka, Mitsui Chemicals, Inc., Japan

Surface hydroxyl groups are essential species in many catalytic reactions. Especially, in oxide surfaces, they play a crucial role in reforming of the surface reactivity due to the adsorption of hydrogen adatoms at oxygen ion (anion) sites. Therefore controlling of the surface hydroxyl on catalysis surfaces is important in the reactivity and the selectivity. As a model surface to control hydroxyl groups, a slightly reduced TiO₂(110) surface was utilized. By repeating many cleaning cycles, surface oxygen atoms on bridge oxygen rows of the TiO₂(110) linearly desorbed, and the line vacancy structures were obtained. The line vacancy was formed by increasing of the density of oxygen vacancies on the TiO₂

surface. After exposing H₂O (1.0 x 10⁻⁴ Pa for 120 s), hydroxyl chain structure, which is linearly arranged hydroxyl groups into two rows on bridge oxygen rows, were formed on the TiO₂(110) surface with the line oxygen vacancy. In-situ NC-AFM measurements at RT to 1.0 x 10⁻⁷ Pa H₂O revealed that the hydroxyl chain structure was formed at the line vacancy site. After H₂O exposure, annealing at above 500 K was sufficient to remove the hydroxyl chains on the TiO₂(110) surface, and then line vacancy structures reappeared on the surface. Before published STM and other experimental results supported that dissociative adsorption of water occurs on oxygen vacancy sites of the TiO₂(110). Therefore these results concluded that the hydroxyl chain structure was formed at the line vacancy site. Thus the formation of the hydroxyl chain structure suggests that controlling of surface hydroxyl groups on catalysis surfaces is possible.

SS-MoP30 Local Nanodeposition of Oxides with Focused Beams - Improving Material and Interface Quality, H.D. Wanzenboeck, M. Fischer, S. Mueller, J. Gottsbacher, W. Brezna, M. Schramboeck, A. Tomastik, H. Stoerti, H. Hutter, E. Bertagnoli, Vienna University of Technology, Austria

The fabrication of silicon oxide by direct-write deposition with a focused beam is an advanced nano-engineering technique. This locally confined chemical vapour deposition is a versatile tool for tailored surface modification. Two alternative methods - deposition with a focused ion beam (FIB) and a focused electron beam (FEB) - are compared. A silicon precursor such as siloxane is adsorbed on the surface and decomposed by the energy of the focused electron or ion beam. The chemical and physical phenomena at the oxide surface were investigated experimentally and by simulation of the energy dissipation of the incident beam. The process stage adsorption, surface diffusion, surface reactions, and layer growth are discussed. This work demonstrates the capability of this maskless method to fabricate arbitrary geometries of oxide and to create real 3-dimensional nanostructures. The material qualities of silicon oxide surfaces obtained with both methods are compared by chemical analysis, vibrational spectroscopy, optical and electrical characterisation. The beneficial addition of oxygen is reported and the optimum process window is identified. The chemical composition and the topography of the oxide surface are investigated by Auger electron spectroscopy (AES) and atomic force microscopy (AFM). A correlation between process parameters and the surface properties was found. The interface between the deposited microstructures is investigated by secondary ion mass spectroscopy (SIMS) and by electrical characterisation of capacitor devices with the deposited silicon oxide. Results indicate significant atomic mixing at the interface with FIB induced deposition, while a sharp interface can be obtained with the electron beam. This work contributes to a fundamental understanding of oxide formation on the nanoscale by beam induced deposition. This emerging maskless nanotechnology promises applications in MEMS, optical microstructures and dielectrics for semiconductor devices.

SS-MoP31 Structure and Growth of Small Au Particles on TiO₂(110), D. Pillay, G. Hwang, The University of Texas at Austin

****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONLY ONE (1) PAPER AT THE CONFERENCE****While Au is known to be chemically inert in its bulk form, nanometer size Au particles dispersed on TiO₂ have been found to exhibit high activities for a variety of catalytic oxidation processes at or below room temperature. Au atoms weakly interact with the TiO₂ surface and become unstable toward sintering in response to changes in the gaseous environment even at moderate temperatures. Given the weak Au-TiO₂ interfacial interaction, Au particle nucleation is thought to predominantly occur at the sites of surface defects, such as (bridging) oxygen vacancies. Similarly, during oxidation processes, a reactant O₂ molecule may adsorb on the vacancy site molecularly or completely heal the defect (while ejecting an oxygen atom). Oxygen species may also interact with Au particles directly or indirectly. Thus, oxygen adspecies can greatly alter TiO₂ surface properties and Au-TiO₂ interfacial interactions, which may in turn influence the nucleation, growth, and sintering of Au particles. In this poster, we will present the results of our recent density functional theory calculations on the interactions between oxygen species and small Au particles on TiO₂(110), with a focus on understanding i) the dynamics of oxygen species on Au/TiO₂ and ii) the effect of oxygen species on Au particle nucleation, growth, and sintering.

Monday Afternoon Poster Sessions, October 31, 2005

SS-MoP32 Gas-Phase Catalytic Processes on Metal-Oxide Supported Gold Nanoparticles, B. Roldan Cuenya, University of Central Florida

Our experimental work aims to improve the understanding of the processes taking place in nanocluster-catalyzed reactions by systematically studying how the nanoparticle size and shape affects its chemical reactivity. For this purpose, the low temperature carbon monoxide oxidation reaction on metal-oxide-supported gold nanoparticles will be used as a model system. Different ex-situ wet chemistry methods such as nanosphere lithography or the self-assembly of metal loaded block-copolymer micelles are being used to create ordered arrays of size- and shape-selected nanospheres, nanorods and triangular nanoprism catalysts. In addition, in-situ (UHV) nanoparticle size and shape modifications by high temperature annealing, Ar⁺ sputtering and O₂-/H₂ plasma treatment are being conducted. Interconnections between directly measurable electronic phenomena and surface chemistry will be established and used to provide insight into catalytic reactions. Temperature-Programmed Desorption (TPD), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), and X-ray Photoelectron Spectroscopy (XPS) are being employed to characterize the changes induced in the metal nanoclusters and their supports upon gas exposure. Our approach relies on the combination of ex-situ size- and shape-selected nanoparticle preparation methods and in-situ reactivity characterization measurements at different stages of well-controlled thermally and chemically induced size and shape transformations.

SS-MoP33 The Preparation and Chemical Reaction Kinetics of Microcrystalline Tungsten Bronze Thin Films with Peroxide and Nitrobenzene Solutions, N.F. Materer, A. Apblett, E.B. Kadossov, K. Khan, E.F. Shams, Oklahoma State University

Microcrystalline tungsten bronze (H_xWO₃) 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 and ultra-violet photoelectron spectroscopy show that these films are indistinguishable from conventionally prepared tungsten bronze powders. In addition, platinum or silver metal is deposited on these films. 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 organic nitrides or peroxides. A satisfactory fit to a kinetic model that involves two simultaneous processes is obtained. The first one is the proton diffusion from the bulk of the film to its surface, and the second is a reaction of the surface proton with the oxidant. In the latter process it is assumed that the surface concentration of the oxidant is effectively constant. The proton diffusion coefficient and the activation energy for the reaction of tungsten bronze films with oxygen gas are also estimated. The addition of catalytic amounts of platinum or silver on the rate is also discussed.

Surface Science

Room 202 - Session SS1-TuM

Vibrational Spectroscopy of Surfaces

Moderator: G.P. Williams, Jefferson Labs

8:20am **SS1-TuM1 Direct Observation of Metathesis Reactions on a Carbide Surface: The Surface Chemistry of Multiple Bonds.**, *M. Sijj, P.H. McBreen*, Université Laval, Canada

Well-defined metal ligand complexes are a feature of organometallic chemistry, and have long served as a guide to understanding chemisorption systems. However, the entire area of metal-ligand multiple bond chemistry appears to have almost no counterpart in surface science. Reports of surface alkylidene species, $M=CR_1R_2$ where M is a single metal atom, are extremely rare. Metal-alkylidenes are catalysts for metathesis chemistry, one of the most powerful synthetic methodologies in modern organic, polymer and materials science. Hence, for a variety of applications, it is very important to develop metathesis chemistry on extended surfaces. An extensive set of surface spectroscopy data will be used to show that alkylidene groups can be prepared and isolated on the surface of molybdenum carbide. Furthermore, it will be shown that vibrational spectroscopy may be used to perform in-situ monitoring of cross-metathesis and ring opening polymerization reactions, isolating both initiator and propagator species. These results illuminate both the reaction mechanism for heterogeneous metathesis and the unique ability of the metal carbide surface to promote highly selective catalysis.

8:40am **SS1-TuM2 Strategies for DFT Modeling of Experimental Surface Vibrational Modes**, *P. Uvdal*, Lund University, Sweden; *M.P. Andersson*, Technical University of Denmark

We have explored and developed electronic structure calculations as a tool for the interpretation of experimental vibrational spectra of surface adsorbates. By combining high sensitive surface infrared spectroscopy and density functional calculations details in the spectra, beyond the harmonic level, can be analyzed. These details allow us to extract new information about the physical properties of adsorbed molecules, information not available using the harmonic or normal mode approximation. For instance the C-H stretch region of organic adsorbates contains often more than 50% of the informational content of the vibrational spectrum. Any proper assignment of this region can, however, not be done at the normal mode level. It requires a treatment, which includes anharmonic coupling between fundamental C-H stretch modes and binary/overtone modes of CH₃ and CH₂ bending modes. This complicates the comparison between calculations and experiments. Base on the concept of spectral moment or intensity weight average one can however obtain the unperturbed frequency of a vibrational mode, e.g. the C-H stretch mode in methoxy. This frequency can then directly be compared to the frequency determined by calculations in the absence of anharmonic coupling between fundamental and binary/overtone modes. This new concept is discussed and related to our recently determined new scaling factor for harmonic vibrational frequencies using the B3LYP density functional method with the triplezeta basis set 6-311+G(d,p)@footnote 1@. @FootnoteText@ @footnote 1@M. P. Andersson and P. Uvdal, J. Phys. Chem. A 109, 2937 (2005).

9:00am **SS1-TuM3 Freidel Oscillations: S and CO Metal Mediated Interactions**, *X.F. Hu, C.J. Hirschmugl*, University of Wisconsin-Milwaukee

The coadsorption of CO and S on Cu(100) is examined to gain a deeper understanding of metal-mediated interactions between co-adsorbates. Using a combination of IRAS, Auger Electron Spectroscopy (AES) and TDMS, we find that CO adsorbates do not occupy the first and second nearest-neighbor adsorption sites of S adatoms, but are strongly bound to third-nearest neighbor sites. Simple site-blocking can explain the absence of CO adsorption at first-nearest neighbor sites. However, we attribute the second- and third-nearest neighbor results to S-induced changes in the LDOS. A local minimum is induced at second-nearest sites, suppressing CO adsorption, but a local maximum at third-nearest sites enhances the C-metal bonding strength. Bonding to these sites is stronger than even on the clean Cu(100) surface. Furthermore, the C-O stretch frequency and the dipole-dipole coupling are affected by the S coverage. For a low S coverage, where dipole-dipole coupling is still dominant, a Coherent Potential Approximation (CPA) treatment of dipole-dipole coupling is used to estimate the spatial extent reffective of S and CO substrate-mediated interactions. reffective is found to be between 6 ~ 7 Å. This work shows

that S affects the CO adsorption in three ways: making adsorption sites electronically unfavorable, affecting the interface bonding between CO and Cu, and reducing the CO intermolecular interaction.

9:20am **SS1-TuM4 Attenuated Total Reflection Infrared Spectroscopy and Nanoparticles: A New Tool for Probing Adsorption (CO, NH@sub 3@) on Planar Model Catalysts (Rh)**, *C.M. Lewis, M.C.M. Van De Sanden*, Eindhoven University of Technology, The Netherlands; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *J.W. Niemantsverdriet*, Eindhoven University of Technology, The Netherlands

Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) is used to study adsorption and/or decomposition of CO and NH@sub 3@ on Rh nanoparticles. The silicon ATR crystal (25 reflections, 45°) with a 50 nm thick hydroxylated thermal SiO@sub 2@ layer acts as the support for the nanoparticles. These are spincoated from a RhCl@sub 3@ solution in water followed by reduction in H@sub 2@ at 200°C. X-ray Photoelectron Spectroscopy (XPS) shows the reduction to Rh@sub 0@ and the removal of Cl. Atomic Force Microscopy (AFM) shows a distribution of 200 particles per μm@super 2@, which are ~3 nm in height. The ATR-FTIR experiments are performed in UHV without exposing the crystal levels and backside (both without oxide and Rh) to the gases. For a 4 cm@super -1@ resolution, a sensitivity of reflectance as low as 5x10@super -5@ absorbance units in the region 2000-3500 cm@super -1@ can be reached. CO exposure validates the detection of species on the nanoparticles, since CO does not interact with the support. Linearly adsorbed CO on Rh is observed at 2023 cm@super -1@. No bridged CO or geminal dicarbonyls are observed. For ammonia, interaction with the silica OH groups is observed around 2900 cm@super -1@ in combination with negative unperturbed OH peaks between 3500 and 3700 cm@super -1@. In addition, N-H bend (1634 cm@super -1@) and stretch (3065, 3197 cm@super -1@) vibrations are observed for substrate temperatures between 20°C and 150°C. The latter correspond to N-H on Rh, as verified with a sample without Rh, and remained after evacuation, suggesting strongly bound species. For 75°C and 100°C, additional peaks at 3354 and 3283 cm@super -1@ are observed, possibly due to NH@sub 2@ intermediates. ATR-FTIR is therefore a powerful technique for probing adsorbates on supported nanoparticles.

9:40am **SS1-TuM5 Formation of C-H and N-H bonds on the Pt(111) Surface as Studied with Reflection Absorption Infrared Spectroscopy**, *R. Deng, E. Herceg, K. Mudiyansele, J. Jones, M. Trenary*, University of Illinois at Chicago

INVITED

The reaction of hydrogen with atomic species adsorbed on transition metal surfaces is a key step in many important catalytic processes. However, many surface probes are not sensitive to hydrogen so the detection and characterization of processes in which hydrogen forms bonds to other elements on surfaces has been difficult. Recent advances in the sensitivity of surface infrared spectroscopy allows surface intermediates with very weak IR absorption bands to be unambiguously detected. It is well known that the complete dehydrogenation of various hydrocarbons eventually leads to graphitic monolayers on platinum surfaces, although the exact forms of the surface carbon prior to graphite formation are still undetermined. Surface carbon has been prepared by the dehydrogenation of ethylene and acetylene on Pt(111) through exposure at 750 K. Subsequent hydrogen exposure leads to clear infrared features due to methylidyne (CH), ethylidyne (CCH@sub 3@), and ethynyl (CCH). These results demonstrate that C atoms and C@sub 2@ molecules exist as stable species on the surface. An ordered (2x2) layer of N atoms can be prepared on Pt(111) through the oxidation of ammonia in which all of the hydrogen and oxygen are removed through the desorption of water. Subsequent hydrogen exposure leads to a sharp and intense infrared band at 3320 cm@sup -1@ due to the NH species. Quantitative determinations of the NH and N coverages through temperature programmed desorption measurements indicate that only a small fraction of the surface N atoms are reactive towards hydrogen. The NH species can not be further hydrogenated to NH@sub 2@ or NH@sub 3@ under the conditions used in these experiments.

10:20am **SS1-TuM7 RAIRS Signature of the Ordered Methyl Bromide Monolayer on Pt(111)**, *I. Samanta, T. Schwendemann*, University of Virginia; *T. Kunstman*, University of Essen, Germany; *I. Harrison*, University of Virginia

Scanning tunneling microscopy (STM) reveals that methyl bromide (CH@sub 3@Br) adsorbed on a Pt(111) surface can order into a relatively close packed monolayer of upright molecules even though the dipole moment of these rod-like molecules is substantial (1.8 Debye in the gas

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phase). The formation kinetics of the ordered (3 x 5) structure can be slow at temperatures less than 100 K. The unit cell contains four CH@sub 3@Br molecules of two kinds oriented with C-Br axis along the surface normal. The CH@sub 3@Br saturation coverage is estimated to be 0.27 ML by STM. Other ordered structures are observed at lower coverages. The evolution of ensemble-averaged reflection absorption infrared spectroscopy (RAIRS), thermal programmed desorption (TPD) spectroscopy, and photochemical dynamics experiments on CH@sub 3@Br/Pt(111) as a function of coverage will be discussed in light of the microscopic structures observed by STM. The RAIRS signature of the ordered CH@sub 3@Br monolayer is the disappearance of the @nu@@sub 5@ asymmetric CH@sub 3@ deformational mode near 1411 cm@super -1@ and the adsorption-site induced splitting of the @nu@@sub 2@ symmetric CH@sub 3@ deformational mode into a doublet at 1271 cm@super -1@ and 1277 cm@super -1@ with fwhms of just 3 cm@super -1@.

10:40am **SS1-TuM8 Adsorption on Carbon Nanotubes Studied Using Polarization-Modulated Infrared Reflection-Absorption Spectroscopy, V.M. Bermudez**, Naval Research Laboratory

Single-wall carbon nanotubes (SWNT's), deposited onto an Al substrate from a liquid suspension, have been cleaned by annealing in UHV. The effects of exposing the sample in situ to atomic H (or D) and/or to DMMP [dimethyl methylphosphonate, (CH@sub 3@O)@sub 2@(CH@sub 3@)P=O] were then studied using polarization-modulated infrared reflection-absorption spectroscopy. Atomic H reacts preferentially near strained or defective regions in the nanotube wall to produce a spectrum consistent with alkane-like species (>CH@sub 2@ and CH@sub 3@). Only a small fraction of the >C=C< sites in the nanotube wall react with H, and there is no clear evidence for monohydride (>C(H)C(H)<) species. For DMMP, data were obtained under steady-state conditions in reagent pressures in excess of half the room-temperature vapor pressure. Adsorption occurs via the P=O group with a coverage that depends on the ambient pressure. Varying the DMMP coverage by changing the pressure causes changes in the spectrum that can be related to the strength of the DMMP/SWNT interaction. Pre-adsorbed H is seen to have little or no effect on the subsequent adsorption of DMMP. For DMMP, the molecular features are superimposed on a broad, smoothly-varying background that can be related to adsorption-induced changes in the Drude parameters characterizing the SWNT free-carrier density and scattering lifetime. Data were also obtained during exposure to @super 16@O@sub 2@ or @super 18@O@sub 2@. As in the case of atomic H, evidence is seen for preferential reaction near strained or defective regions, but no vibrational modes of adsorbed O or O@sub 2@ are detected.

11:00am **SS1-TuM9 Nanoporous Gold As a Novel Highly Active Substrate for Surface-Enhanced Raman Spectroscopy, J. Biener, J.R. Hayes, S.O. Kucheyev, T. Huser, C.E. Talley, A.M. Hodge, A.V. Hamza**, Lawrence Livermore National Laboratory

Surface-enhanced Raman-scattering (SERS) spectroscopy has attracted considerable interest in recent years due to the possibility to reach the single molecule detection limit. Colloidal solutions of gold or silver with particle sizes in the submicron range are most commonly used as SERS active substrates. However, the limited stability and reproducibility of metal colloids currently hampers their use as SERS substrates. Here, we report on the development of nanoporous gold (np-Au) as a novel, highly active SERS substrate. The SERS activity was probed using crystal violet as a test molecule. The significant Raman enhancement observed seems to be a consequence of the nanoscale surface roughness and curvature of np-Au. The material is prepared by dealloying Ag-Au alloys, and exhibits an open sponge-like morphology of interconnecting Au ligaments with a typical pore size distribution on the nanometer length scale. The dimensions of both pores and ligaments can be further fine-tuned by chemical and/or thermal treatments. Our ultimate goal is the development of an affordable, stable, reproducible, and highly active substrate for SERS-based chemical sensors. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

11:20am **SS1-TuM10 Vibrational and Photoelectron Spectroscopy of Formic Acid and Water Coadsorbed on Au(111) Surfaces: Chemical Interaction and Compound Formation, G. Pirug, M. Kazempoor**, Forschungszentrum Jülich GmbH, Germany

The coadsorption of formic acid (HCOOH) and water (H@sub 2@O) has been studied on Au(111) single crystal surfaces by means of vibrational spectroscopy (HREELS) and photoelectron spectroscopy (XPS) in the temperature range between 90 K and 200 K. Formic acid adsorbs at 90 K

molecularly with vibrational modes characteristic for solid formic acid. Annealing results in a complete desorption at 190 K. Upon sequential adsorption of formic acid and water at 90 K no significant chemical interaction can be deduced from the vibrational signatures and the core level photoelectron binding energies. Independent of the sequence of exposure coadsorption or layered growth without intermixing is observed in the monolayer and the multilayer regime, respectively. Heating of the coadsorbed layer to about 140 K results in the formation of a new surface complex with characteristic vibrational losses at 190, 590 and 1000 cm @super -1@. Based on these frequencies and supported by the corresponding stoichiometries as deduced from XPS possible compounds will be discussed. Upon further annealing this complex decomposes leaving only molecularly adsorbed formic acid on the surface at 160 K. These results will be discussed in the light of recent findings for the electrochemical oxidation of formic acid on Au surfaces.

11:40am **SS1-TuM11 STS Vibrational Study of 1,3-cyclohexadiene on Si(100) Surface, B. Naydenov, J.J. Boland**, Trinity College Dublin, Ireland

Scanning tunnelling spectroscopy was performed on 1,3-cyclohexadiene modified Si(100) surface at 5K. Degenerated N-type semiconductor and platinum covered tungsten tips were used. For the first time a vibrational spectrum of chemisorbed molecule on semiconductor surface was obtained. The spectroscopic conditions involved small tip-sample separations, far from the normal imaging conditions, and for which the simple tunnelling picture involving overlapping wave function tails is no longer valid. Under such conditions significant forces and weak chemical bond occurs between the tip and the surface. The vibrational features and the tunnelling barrier height variations with the tip-sample distance will be discussed.

Surface Science

Room 203 - Session SS2-TuM

Defects on Oxide Surfaces

Moderator: D. Bonnell, University of Pennsylvania

8:20am **SS2-TuM1 Structure and Properties of SrTiO@sub 3@ (100) Surface, R. Shao, M. Nikiforov, D. Bonnell**, University of Pennsylvania

The surfaces of Strontium Titanate, one of the simplest perovskites, have been intensively studied because of its relevance to catalysis, environmental interactions and electronic devices. The (100) surface can terminate in either Sr-O or Ti-O planes. A number of reconstructions have been found on this surface depending on processing conditions. We have been able to stabilize atomically smooth (100) surfaces with unit cell (0.4 nm) and half unit cell (0.2 nm) steps assuring the presence of both types of terminations. Scanning tunneling spectroscopy of the two termination planes exhibits differences in electronic structure that are related to the proximity of Ti d orbitals near the surface. An orientational relationship between reconstructions and step edge direction is quantitatively related to strain from a systematic series of surfaces with different miscut angles. Finally the surface relaxation and electronic structure at low temperatures will be presented.

8:40am **SS2-TuM2 Oxygen Adsorption, Diffusion, and Reaction on a Reduced TiO@sub 2@(110) Surface, D. Pillay, G. Hwang**, The University of Texas at Austin

The rutile TiO@sub 2@(110) surface has been widely used as a catalyst for photochemical reactions and a support for transition metal catalysts. Molecular oxygen adsorption plays an important role in determining the activity of TiO@sub 2@ and supported metal catalysts. Surface bound oxygen species may directly influence chemical and photochemical processes occurring on TiO@sub 2@. In addition, O@sub 2@ exposure leads to significant structural changes of supported metal particles, which may in turn affect their catalytic activity. It has been found that O@sub 2@ adsorbs on TiO@sub 2@(110) only when O-vacancies are present. Despite its importance, however the chemistry and dynamics of adsorbed oxygen species on a Au-covered reduced TiO@sub 2@(110) surface are still unclear. Using density functional theory calculations, we have investigated the adsorption and diffusion of oxygen species on the reduced TiO@sub 2@(110) surface. We have found that O@sub 2@ strongly binds not only to O-vacancies, but also to Ti(5c) neighbors, due to delocalization of unpaired electrons arising from the removal of neutral bridging oxygen atoms. Our results show that O@sub 2@ can jump across an oxygen vacancy and diffuse along a Ti(5c) row, with a moderate barrier that is significantly altered by the density of O vacancies. Based on our calculation results, we

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will discuss the diffusion and healing of O vacancies associated with O@sub 2@ adsorption, as a function of the vacancy density. We will also present the structure and energetics of higher coverage O@sub 2@ adsorption, as well as CO oxidation mechanisms on the reduced TiO@sub 2@(110) surface.

9:00am **SS2-TuM3 High-Resolution Scanning Tunneling Microscopy Studies of Surface Reactions on Rutile TiO₂(110), F. Besenbacher, University of Aarhus, Denmark** **INVITED**

Transition-metal oxide surfaces play an important role in a wide range of applications, e.g. heterogeneous catalysis, photoelectrolysis, biocompatibility and sanitary disinfection. Defects like oxygen vacancies often dominate electronic and chemical properties of transition-metal oxide surfaces. In recent studies on a prototypical model oxide system (rutile TiO₂(110) surface) we exploited our high-resolution, variable-temperature and fast-scanning Aarhus STM to study how oxygen vacancies influence surface and interface reactions. Water dissociation on TiO₂ is of fundamental interest as an example of a simple surface chemical process with important applications. In high-resolution STM experiments, we unambiguously identify surface oxygen vacancies and hydroxyl groups. Controlled voltage STM pulses allow us to desorb OH groups only; O vacancies remain unaffected. Through STM images and time-resolved movies, we determine the active site responsible for the water molecule dissociation on TiO₂(110). At low H₂O exposures, O vacancies dissociate water molecules by transferring one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy. At elevated exposures, a novel water dissociation channel is seen and will be described in detail. The amount of water dissociation is not limited by the density of oxygen vacancies on the clean surface as proposed earlier in literature. Extended oxygen exposure on TiO₂(110) will lead to stoichiometrization of the support, thus markedly reducing its reactivity. An atomic-scale understanding of the healing process is still lacking, but it is thought to be a simple mechanism where a single O₂ molecule heals two vacancies subsequent to a dissociative process. Using high-resolution STM and TPD measurements, we investigate the interaction of O₂ from the gas phase with different surface defects (O vacancies, OH groups) on TiO₂(110).

9:40am **SS2-TuM5 Surface Reconstruction Variations on Barium Titanate (100), R. Shao, D. Bonnell, University of Pennsylvania**

BaTiO@sub 3@, is a prototype ferroelectric compound and a simple model for interactions in complex oxides. Recently the effect of ferroelectric dipoles on interactions of surfaces has been examined as it relates to domain specific chemical reactivity. Scanning probe microscopy is the obvious probe of local surface reactions; however, it has proven difficult to obtain reproducible atomically smooth surfaces because of its tendency toward non stoichiometry and carbonate formation. In this work, we have determined the sequence of high temperature annealing in oxidizing and reducing atmospheres with which BaTiO@sub 3@ (100) surfaces can be produced with unit cell (0.4 nm) and half unit cell (0.2) step heights. These steps correspond to different lattice plane terminations. Atomic resolution STM is used in conjunction with LEED/AES and Scanning Surface Potentiometry (Kelvin Probe Microscopy) to compare the geometric and electronic structures that occur on these surfaces as a function of thermal history. Differences in electronic structure determined from tunneling spectroscopy are compared to theoretical predictions.

10:00am **SS2-TuM6 Defects Modeled with Vicinally-Stepped Oxide Surfaces: the Adsorption of Bromobenzene on NiO(100), E.M. Marsh, S.C. Petitto, M.A. Langell, University of Nebraska-Lincoln**

The chemical reactivity of a metal oxide surface is often dominated by its defect properties. However, at naturally-occurring levels these defects are often present in low concentrations and as only one of a range of defect types making their effect on surface reactivity difficult to isolate. We have modeled oxide step defects with periodically-stepped NiO(100) substrates, where the predominant defect type and concentration can be readily controlled, and have investigated the ability of the stepped substrates to adsorb and dissociate bromobenzene (C@sub 6@H@sub 5@Br). The surfaces were characterized using Auger electron (AES) and x-ray photoelectron (XPS) spectroscopies, low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and thermal desorption mass spectrometry (TDS). In particular, the geometry of the adsorbate is correlated with short terrace widths and this in turn affects the dissociative nature of the adsorbate interaction.

10:20am **SS2-TuM7 Structure, Defects, and Adsorption on Metal Oxide Surfaces, U. Diebold, Tulane University** **INVITED**

In recent years, the surface science of metal oxides has experienced a remarkable increase in terms of research papers published, systems studied, and level of detail of the obtained information. A long-standing paradigm -- that surface defects on oxides are dominant reactivity centers - is now scrutinized with scanning probe techniques. In this talk, I will give a representative overview of surface structural and adsorption studies on various surface orientations of TiO@sub 2@, ZnO, and SnO@sub 2@. Our experimental investigations are significantly enhanced through collaborations with theoretical groups.

11:00am **SS2-TuM9 Controlling Surface Reactivity of SnO@sub 2@(101): Dissociative and Molecular Water Adsorption, M. Batzill, U. Diebold, Tulane University**

Water adsorbs dissociatively on many oxide surfaces. In such cases undercoordinated surface oxygen atoms accept a proton and the remaining water-OH- adsorbs on surface cation sites. Thus the surface reactivity towards water dissociation may be tuned by controlling the number of undercoordinated surface oxygen atoms (Broensted base sites). On SnO@sub 2@(101) such a control over the surface composition can be exerted and the surface can be prepared with and without terminating oxygen atoms.@footnote 1@ Here we show by valence band photoemission that these two surfaces show different activity towards water adsorption. Surfaces without bridging oxygen adsorb water weakly while dissociation is observed on surfaces exhibiting terminating oxygen. The different activity of the surfaces is also apparent from water induced band bending. Dissociative adsorption causes downward band bending of ~0.35 eV which consequently causes a large increase in the surface conductivity of the SnO@sub 2@ sample. The latter is measured using a novel approach utilizing surface charging as a conductivity probe. @FootnoteText@ @footnote 1@ M. Batzill, A.M. Chaka, U. Diebold, Europhys. Lett. 65, 61 (2004).

11:40am **SS2-TuM11 The Reaction of Water over the Stoichiometric and Defected Surfaces of Uranium Dioxide: a High Resolution XPS Study, S.D. Senanayake, G.I.N. Waterhouse, The Univ. of Auckland, New Zealand; A.S.Y. Chan, Rutgers, The State Univ. of New Jersey; D.R. Mullins, Oak Ridge National Lab.; T.E. Madey, Rutgers, The State Univ. of New Jersey; H. Idriss, The Univ. of Auckland, New Zealand**

The chemistry of the uranium oxides is complex and historically been important to many aspects of nuclear technology. A recent study has shown using XPS that argon ion sputtering of the UO@sub 2@ surface can form a stable reduced oxide surface (UO@sub 2-x@) due to creation of oxygen defects.@footnote 1@ This work uses high resolution photoelectron spectroscopy (HRXPS) performed at the beam line U12a at the National Synchrotron Light Source/BNL to investigate the effect of this defect formation process. Sputtering at 300 and 95K gave different defect distributions. The reduced surface has a complex set of oxidation states lower than that of U@super +4@ including U metal (U@super 0@). Previous investigations made on the reactivity of water vapor on polycrystalline UO@sub 2@ and defected single crystal UO@sub 2-x@ surface have revealed complex reaction pathways to the production of H@sub 2@ and XPS has further confirmed adsorbate induced oxidation of the surface.@footnote 1@ This work aims to further examine the effect of D@sub 2@O adsorption on the stoichiometric and sputter reduced surfaces of UO@sub 2@ at 300 and 95K. The effects of the thermal chemistry and oxidation of the surface is studied using temperature programmed XPS (TPXPS). In particular, the formation of D@sub 2@O ice at low temperature and dissociated OD species versus the role of defects in this heterogeneous interplay is examined. @FootnoteText@ @footnote 1@ Senanayake S.D., Idriss H., Surf. Sci. 563 (2004) 135.@footnote 2@ Senanayake S.D., Rousseau R., Colegrave D., Idriss H, J. Nucl. Mater. In press.

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Surface Science

Room 202 - Session SS1-TuA

Compound Semiconductors

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS1-TuA1 Doping Semiconductor Nanocrystals, S.C. Erwin**, Naval Research Laboratory; *L. Zu*, U. Minnesota; *M.I. Haftel, A.L. Efros, T.A. Kennedy*, Naval Research Laboratory; *D.J. Norris*, U. Minnesota **INVITED**
Doping—the intentional introduction of impurities into a material—is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated similar efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes, many of these efforts have failed, for reasons that remain mysterious. For example, individual Mn atoms can be incorporated into nanocrystals of CdS and ZnSe, but not into CdSe—despite comparable solubility limits near 50 percent in the bulk crystals. These difficulties have hindered the development of important new materials, including p- and n-type, and even magnetic, nanocrystals. Such failures have often been attributed to "self-purification," an allegedly intrinsic mechanism in nanocrystals whereby impurities are expelled to the nearby surface. Here we propose a very different view: that doping is controlled instead by the initial adsorption of impurities on the nanocrystal surface during growth. We show that impurity adsorption—and therefore doping efficiency—is determined by three main factors: the surface morphology of the nanocrystal, its overall shape, and the tendency of surfactants in the growth solution to bind the impurity. Calculated Mn adsorption energies and equilibrium shapes for several cubic and hexagonal nanocrystals lead to specific doping predictions. These are confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Finally, we use our predictions to incorporate individual Mn impurities into previously undopable CdSe nanocrystals. This success establishes that earlier difficulties with doping are not intrinsic, and suggests that a variety of doped nanocrystals—for applications from solar cells to spintronics—can be anticipated.

2:40pm **SS1-TuA3 Scanning Tunneling Microscopy Study of Square Manganese Tetramers on Mn₃N₂(001), R. Yang, H.Q. Yang, A.R. Smith**, Ohio University

The growth of transition metal nitride layers has been a subject of significant interest due to their unique electronic, magnetic, and structural properties. We have previously investigated the growth of Mn₃N₂ on MgO(001) by molecular beam epitaxy (MBE). Mn₃N₂ is a layer-wise antiferromagnet with magnetic moments of ~ 3 μ_B. Two orientations ((010) and (001)) of this structure were grown controllably on MgO(001), depending on the growth conditions. As the bulk structure corresponds to 2 layers of Mn followed by 1 layer of N in a fct arrangement, scanning tunneling microscopy (STM) shows that the (010) surface consists of row structures. These rows correspond to the Mn planes, which are perpendicular to the surface. Here we present results for the (001) surface in which the Mn planes are in the surface plane. However, this presents an interesting question regarding the epitaxial Mn₃N₂ (001) growth surface, due to the Mn-N-Mn-N-Mn stacking sequence of the atomic layers in bulk. If the stacking sequence extends to the surface, then different structures should be observed on adjacent terraces. Again, these films are grown on MgO(001) substrates by MBE. STM images show smooth terraces and atomic steps. On certain of the terraces a unique and new reconstruction is seen, resolved as square Mn tetramers in a c(4x2) structural arrangement. Two domains of the tetramer reconstruction, rotated by 90 deg to each other, occur. A model is presented for this square Mn tetramer reconstruction, in which the Mn atoms of the tetramer layer belong to the Mn layer at the surface in the Mn-N-Mn-N-Mn stacking sequence. @FootnoteText@ @footnote 1@Yang et al., J. Appl. Phys. 91(3), 1053 (2002). @footnote 2@G. Kreiner, and H. Jacobs, J. Alloys and Comp. 183, 345 (1992). @footnote 3@Yang et al., Appl. Phys. Lett. 78, 3860 (2001).

3:00pm **SS1-TuA4 Investigations of Surface Reconstructions and 3D Roughening in InGaAs Films, L.E. Sears, J.M. Millunchick**, University of Michigan; *C. Pearson*, University of Michigan - Flint

The epitaxial growth of III-V semiconductors and their corresponding properties depend on the surface reconstructions and morphology of the film grown. We have found that the surface structure of In_xGa_{1-x}As alloys consists of multiple surface reconstructions

depending on the composition x. The goal of this work is to determine which reconstructions are present as a function of both composition and temperature, in order to map out the surface phase diagram for this system. For example, for In_{0.81}Ga_{0.19}As/InP grown at 503°C with an As overpressure of 2.1 ML/sec and a growth rate of 1.16 ML/sec, highly ordered regions of (2x4) coexist with more disordered regions having a (4x3) symmetry. In this case, the percentage of (2x4) covering the surface initially increases with increasing thickness, followed by a sharp decrease that corresponds to the onset of surface roughening and 3D roughening. Previous work on In_{0.27}Ga_{0.73}As/GaAs, which has a similar lattice mismatch, shows similar disordered (4x3) regions, but the highly ordered (2x4) regions have been replaced by (2x4) regions. @footnote 1@ It is postulated that the (4x3) surface reconstruction is a unique alloy structure, while the (2x4) reconstructions are enriched in In. @FootnoteText@ @footnote 1@ Millunchick JM, Riposan A, Dall B, Pearson C, and Orr BG, Surf. Sci. 550 1(1-3): 1-7 FEB 10 2004.

3:20pm **SS1-TuA5 SiO₂/GaAs Charge Build Up Induced Pinning, D.L. Winn, M.J. Hale**, University of California, San Diego

The correlation between atomic bonding sites and the electronic structure of SiO₂ on GaAs(001)-(2x8)/(2x4), was investigated using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT). At low coverage, STM images reveal that SiO₂ molecules bond Si-end down; this is consistent with Si being under-coordinated and O being fully-coordinated in SiO₂. At ~5% monolayer (ML) coverage, multiple bonding geometries were observed. To confirm the site assignments from STM images, DFT calculations were used to estimate the exothermicities of the different bonding geometries. However, the sites predicted to be most stable were not the most abundant sites observed in the STM experiments. To rectify the discrepancy between calculations and experiments, a total energy vs. SiO₂ chemical potential plot (i.e. SiO₂ coverage) was constructed. Once the bonding geometries were deduced, STS measurements were performed, which showed that SiO₂ pins the Fermi level at ~5% ML coverage. Density of state (DOS) and partial density of state (PDOS) calculations revealed that only certain bonding geometries pin the Fermi level.

3:40pm **SS1-TuA6 Phosphine and Tertiarybutylphosphine Adsorption on the Indium-Rich InP (001)-(2x4) Surface, R.L. Woo, S.F. Cheng, G. Chen, Y. Sun, R.F. Hicks**, University of California, Los Angeles

Phosphine (PH₃) and tertiarybutylphosphine (TBP) are widely used as the group V sources during the MOCVD growth of P-containing compound semiconductors and their alloys. The kinetics of PH₃ and TBP adsorption and phosphorus desorption from InP (001) have been studied using optical techniques and reflectance difference spectroscopy. It is found that the sticking probability of TBP decreases from 0.007 to 0.001 with increasing temperature from 420 to 520 °C; whereas the sticking probability of PH₃ is approximately equal to 0.001 over the same range. In this report, we present a vibrational study of TBP and PH₃ adsorption on the indium-rich InP (001)-(2x4) surface. Both molecules form a dative bond to exposed indium atoms on the surface. A fraction of these species decompose to PH₂ or PH species with hydrogen and tertiarybutyl ligands transferring to nearby phosphorus sites. The initial datively bonded state explains the low sticking probability of these molecules, as reversible desorption competes effectively with irreversible dissociative adsorption at elevated temperatures.

Surface Science

Room 203 - Session SS2-TuA

Tribology, Adhesion and Friction

Moderator: K.J. Wahl, Naval Research Laboratory

2:00pm **SS2-TuA1 Temperature Dependence of Nanoscale Friction, A. Schirmeisen, L. Jansen, H. Fuchs**, University of Muenster, Germany

Friction processes at the nanoscale are the focus of numerous research projects, yet a comprehensive picture is still lacking. Despite the fact that most of the proposed models for energy dissipation in point contacts inherently depend on the sample temperature, this issue has been rarely addressed in experimental work. In this contribution we present nanoscale friction experiments with an ultrahigh vacuum atomic force microscope (AFM), where the sample temperature was varied by two orders of magnitude from 30 K to 300 K. Two different materials have been investigated: Graphite and silicon. On HOPG graphite atomic scale "stick-

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slip" is typically observed. Tribological properties of silicon contacts are of great interest in the area of MEMS/NEMS technology, where friction and wear are an important issue for the technical application of these devices. On graphite the overall friction increases monotonically when lowering the sample temperature. This behaviour can be understood in the framework of atomic scale "stick-slip" friction. The temperature influences the probability of the tip to jump between adjacent potential minima, in effect causing friction to decrease with increasing temperature. In contrast, the friction temperature curves on silicon show a rather complex behaviour, with a pronounced friction maximum at 100 K. Similar peaks have been found before in experiments, where internal friction properties of macroscopic vibrating silicon membranes were measured. Those so-called "Debye-peaks" are related to thermally activated creation of defects in the bulk material, which leads to a strong enhancement of energy dissipation at the Debye temperature. We will discuss some of the intriguing similarities between our nanoscopic friction measurements and the concept of the Debye-peaks in bulk material. In Sang et al., Phys. Rev. Lett. 87 (2001) 174301. In Berry and Pritchett, J. Appl. Phys. 67 (1990) 3661.

2:20pm SS2-TuA2 Capillary Adhesion and Tribology involving Adventitious Water on SiOx Surfaces, J.E. Houston, Sandia National Laboratories

Thin water films adsorbed on surfaces are very important in interfacial interactions and can be critical in determining the behavior and stability of MEMS and NEMS-type devices, which are dominated by extremely high surface to volume ratios. In this presentation, the results of a study are discussed concerning the interfacial interaction of a silica tip and an O-H terminated SiOx surface as a function of both temperature and relative humidity. The study utilizes Interfacial Force Microscopy (IFM) and involves measurements of the normal and frictional forces as a function of interfacial separation. The results indicate, even at very low humidities, that the force profiles are characteristic of a capillary interaction. In addition, the behavior of the lateral force shows significant levels of friction upon capillary formation, increasing further as the two surfaces approach. Upon separating the surfaces, a small hysteretic behavior is observed but with little indication of the "snap-out" instability normally associated with meniscus rupture. These measurements are repeated as a function of tip speed, relative humidity and temperature in order to gain insight concerning the thickness of the water layers, their viscosities and the rates of capillary condensation and evaporation. These results are contrasted with those from similar experiments involving self-assembled monolayer films terminated by combinations of -CH3 and -COOH end-groups. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:40pm SS2-TuA3 Aqueous Based Lubrication: Fundamental Studies of Polymer Brushes Adsorbed at Oxide Surfaces, S.S. Perry, X. Yan, University of Houston; N. Spencer, S. Lee, M. Mueller, Swiss Federal Institute of Technology, Switzerland

The development of synthetic polymer lubricants to mimic joint lubrication within the human body will be presented. Unlike most industrial applications involving oils and greases, lubrication of these joints is accomplished in an aqueous environment. Fundamentally, water is a poor lubricant in most settings due to the weak pressure dependence of its viscosity, yet the contacting surfaces of skeletal joints function with low friction throughout a lifetime. Motivated by the molecular structure of materials making up joint surfaces, interfacial friction between polymer brush surfaces under aqueous environments has been probed with an array of molecularly sensitive surface analytical techniques including atomic force microscopy. The brush surfaces, comprised of poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), have been generated through the spontaneous adsorption of polymer from solution onto oxide substrates and sodium borosilicate surfaces (AFM tip). The character of the polymer films has been investigated in-situ with the quartz crystal microbalance (QCM) and atomic force microscope (AFM) and ex-situ with ellipsometry and X-ray photoelectron spectroscopy (XPS). The interfacial friction measurements have been carried out on polymer-coated substrates with bare or polymer-coated, microsphere-attached tips in over a range of solution conditions. It was found that the adsorption of polymer on oxides strikingly reduced the interfacial friction, resulting in ultra-low friction under certain conditions. By using a series of PLL-g-PEG polymers differing from each other in PEG side-chain length and grafting ratio, we observed that frictional properties of polymer-coated interfaces strongly depend on the architecture of PLL-g-PEG. Polymer-film formation and the influence of

polymer architecture will be reviewed while the role of solvent and manifestation of ultra-low friction will be discussed in detail.

3:20pm SS2-TuA5 Molecular Dynamics Simulations of the Nanotribological Behavior of a Polytetrafluoroethylene Transfer Films, I. Jang, W.G. Sawyer, S.R. Phillpot, S.B. Sinnott, University of Florida

Mechanical devices for space applications need to be able to operate reliably in an extreme range of environments. Therefore, the physical and chemical integrity of the materials has to be assured under extremes of both high and low temperature, under ambient pressures and in near absolute vacuum, and under solar radiation. Polytetrafluoroethylene (PTFE) is known to have good thermal and chemical stability, and a low frictional coefficient. Thus polymer nanocomposites based on PTFE are considered to be promising materials for solid lubricant in aerospace applications. Like other polymer materials, many properties of PTFE depend on morphology. By changing the polymeric chain structure and combining it with other materials, it is likely that the frictional coefficient of PTFE can be made lower and its wear resistance further improved. In order to develop new material systems with superior frictional properties or to improve the existing ones, it is necessary to understand the detailed mechanisms of their frictional behavior, and the effect of molecular structure on friction. In this study, molecular dynamics (MD) simulations are performed to examine the effect of chain configuration on the frictional behavior of PTFE at the molecular level, with the aim of identifying the fundamental wear mechanisms, and guiding the further refinement of the materials with low frictional coefficients for space applications.

3:40pm SS2-TuA6 Correlation of Frictional and Thermal Properties with Molecular Chain Order in Self-Assembled Monolayers of Organosilanes on Silicon, S. Sambasivan, National Institute of Standards and Technology; S. Hsieh, National Institute of Standards and Technology; D.A. Fischer, S. Hsu, National Institute of Standards and Technology

n-Alkyltrichlorosilanes films with different chain lengths (Cn films where n=5-30) were characterized by Near edge x-ray absorption fine structure (NEXAFS), FTIR and AFM. The information afforded from these complementary techniques has provided the unique opportunity to interpret the frictional properties of the monolayer films in relation to the molecular assembly and chain lengths. In this study, we use the non-destructive x-ray absorption technique NEXAFS to quantitatively measure the surface (~6nm) molecular orientation of SAMs (self-assembled monolayers). We observe that the chain lengths having 12, 16 and 18 carbon atoms are highly oriented with a preferential molecular orientation of the polymeric C-C chains perpendicular to the surface. C5 and C30 SAMs did not exhibit preferential orientation of the alkyl chain and C10 showed partial ordering. Complimentary FTIR studies were done to estimate order qualitatively by peak positions of asymmetric CH2 and the symmetric CH2 stretches. The molecular order information from FTIR followed similar trends as determined by NEXAFS. The frictional properties of the organic monolayers were determined through the simultaneous measurement of normal (load) and lateral (friction) interfacial forces with AFM. Friction measurements on different chain lengths follows similar trends with surface order calculated from NEXAFS. In-situ heating and NEXAFS experiments on C16 films reveal that C16 film were well ordered up to 200°C and heating beyond that temperature it transitions from partially ordered to completely disordered/destroyed at 350°C. AFM images show a significant change in surface morphology after annealing. Friction force measurements indicated an increase after heating to 350°C, values approaching close to the friction forces from bare Si wafer. Our results show that the degree of ordering in the SAM governs the friction properties of the film.

Surface Science

Room 206 - Session SS3-TuA

Ultrafast Surface Dynamics

Moderator: I. Harrison, University of Virginia

2:00pm SS3-TuA1 Probing Molecular Motion Induced by Femtosecond Laser Pulses on a Site-by-Site Basis with Scanning Tunneling Microscopy, L. Bartels, University of California, Riverside; F. Wang, D. Moeller, Columbia University; E. Knoesel, Rowan University; T.F. Heinz, Columbia University

The fundamental time scale for nuclear motion and energy flow in surface dynamics lies in the femto- to picosecond range. With the on-going advances in laser technology, many powerful new approaches have been

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developed to explore the dynamics of elementary surface processes directly in the time domain. In this paper, we present an application of femtosecond laser radiation to examine the dynamics of the elementary process of surface diffusion. To this end, femtosecond laser irradiation is used to excite adsorbed CO molecules on a Cu(110) surface; the ensuing motion of individual molecules across the surface is characterized on a site-to-site basis by in-situ scanning tunneling microscopy (STM). Adsorbate motion both along and perpendicular to the rows of the Cu(110) surface occurs readily, in marked contrast to the behavior seen for equilibrium diffusion processes. In addition, STM permits us to determine the rate of the concurrent laser-induced desorption process. The experimental findings for the efficiency and direction of the molecular motion can be understood as a manifestation of strong coupling of the lateral degrees of freedom of the adsorbed molecules to the substrate electronic excitation produced by the femtosecond laser radiation. The overall efficiency for surface diffusion is modeled using data on the thermal diffusion of CO/Cu(110) in conjunction with a description of coupling of the frustrated translational mode to the electronic and lattice excitation of the substrate. The dominant role of the substrate electronic excitation emerges from this analysis. The experiment represents a successful combination of the capabilities of ultrafast laser radiation for accessing non-equilibrium phenomena and the capabilities of STM for accessing the atomic length scale. Possible future research directions will be discussed.

2:40pm **SS3-TuA3 Ultrafast Laser Modification of Single Crystal MgO Surfaces**@footnote 1@, *J.T. Dickinson, S.C. Langford*, Washington State University; *W.P. Hess*, Pacific Northwest National Laboratory; *L.A. Boatner*, Oak Ridge National Laboratory

Interactions between wide bandgap insulators and nanosecond pulses of laser light at sub bandgap wavelengths often require defects for both absorption and emission. With ultrafast pulses, multiphoton absorption across the bandgap is much more probable and often yields exciton mediated decomposition. The doubly charged lattice of materials like MgO strongly inhibits exciton-induced decomposition. We compare the response of (100) MgO to 100 fs pulses at wavelengths of 800, 400, and 267 nm with our earlier studies using nanosecond pulses at 248 nm and 193 nm, where the latter interactions were clearly defect-mediated. Surfaces modified by femtosecond pulses show evidence for both photothermal and photoelectronic processes when examined by AFM and SEM. Some of these processes are clearly mediated by defects. @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

3:00pm **SS3-TuA4 Wavelength-Dependent Infrared Laser Induced Hydrogen Desorption from a Si(111) Surface**, *Z. Liu*, University of Minnesota, Vanderbilt University; *P.I. Cohen*, University of Minnesota; *L.C. Feldman, N.H. Tolk*, Vanderbilt University; *Z. Zhang*, Oak Ridge National Laboratory

Wavelength-dependent infrared laser induced hydrogen desorption from a Si(111) surface hydrogen passivation on silicon surfaces is a bottleneck in low temperature Si homoepitaxy. We employ infrared laser radiation from the Vanderbilt Free-Electron Laser to desorb hydrogen from a Si(111) surface at a temperature below 300C where thermal effects are minimal. The vibrational mode of the Si-H bond was excited by the infrared laser to enhance hydrogen desorption. The cross-section of the coupling between the laser and the Si-H bonds has been measured as a function of laser wavelength and power, showing a resonant effect at the energy of the vibrational mode at 2087 cm@super -1@. The desorption rate was maximized when the polarization of the light was maximized along the Si-H bond direction. The vibrational energies of the Si-H bond are different at terrace sites and step sites. Thus this mechanism provides a way to selectively desorb hydrogen atoms from different locations on the Si surface, and allows site-selective epitaxial growth of Si. To our knowledge this is the first report of wavelength-selective desorption of an adsorbate on a semiconductor surface. This project is partially supported by DARPA/SPAWAR grant N66001-04-1-8924 and DOE grant ER45781.

3:20pm **SS3-TuA5 Surface Plasmon Oscillation in Gold Nanocrystals of Different Shapes: Some Radiative and Nonradiative Ultrafast Properties**, *M. El-Sayed*, Georgia Institute of Technology **INVITED**

The surface plasmon oscillation in gold nanocrystals will be introduced and its enhancement of the absorption, fluorescence and scattering properties will be discussed as a function of shapes. Excited with femtosecond lasers, the electronic oscillation rapidly relaxes into phonon excitation. The lattice oscillation can be detected optically as it modulates the surface plasmon absorption (the color) of the nanocrystals. The dependence of this oscillation on size, shape and interparticle coupling will be discussed

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Room Exhibit Hall C&D - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Varying the Interfacial Structure of Alkanethiol Monolayers on Gold Through Controlled Thermal Desorption, C.D. Zangmeister, L.B. Picraux, National Institute of Standards and Technology

This study investigates the formation of low-density, flat-lying decanethiol chemisorbed on Au prepared by heating the surface covered with a densely-packed, upright monolayer to a surface temperature above the onset of desorption. We determined conditions for preparing the low-density phase of decanethiol by observing the evolution of the surface and interfacial structure as a function of the surface temperature using polarized ultraviolet photoemission spectroscopy. The preparation conditions were similar for single- and polycrystalline gold surfaces. Once the low density decanethiol phase was formed, reflection absorption infrared spectroscopy was utilized to determine the orientation of the carbon chain backbone with respect to the Au surface.

SS-TuP2 Ultrastable Conductance Measurements of Self-Assembled Monolayer Supported Phenylene-Ethylene Oligomers, S.U. Nanayakkara, M.M. Blake, A.A. Dameron, R. Zhang, C. Pochas, M. Kim, P.S. Weiss, The Pennsylvania State University; T.P. Pearl, North Carolina State University; S. Uppili, D. Allara, The Pennsylvania State University; J.M. Tour, Rice University

We have used alkanethiolate self-assembled monolayers (SAMs) to fabricate support matrices for probing the charge transport properties of both isolated and bundled phenylene-ethylene oligomers (OPEs). By utilizing solution- and vapor-phase manipulation techniques, we can select the distribution of the OPE molecules within the SAM matrix. These fabrication techniques, in combination with the spatial and energy resolution afforded by low temperature scanning tunneling microscopy and spectroscopy, have enabled us to probe the electronic properties of these molecules. We have probed individual substituted OPE molecules in analogous environments to understand the effects of chemical substitution on charge transport. We aim to understand the conductance pathways of these molecules as a function of their chemical structure, physical environment and adsorption site.

SS-TuP3 Geometric and Electronic Structure of Self-Assembled Monolayers on Noble Metal Surfaces: Dodecanethiol on Au, Ag, and Pt, T.M. Sweeney, J.M. Burst, P.S. Robbert, J.W. Hobson, S.M. Huston, C.A. Ventrice, Jr., University of New Orleans; B. Hayes, H. Geisler, Xavier University

Self-assembled monolayers (SAMs) have been grown by vapor deposition in UHV and by solution growth in ambient conditions on Au(111), Ag(111), Pt(111), and Pt(100) surfaces. The geometric structure of the SAMs has been studied with low energy electron diffraction (LEED), and the electronic structure has been measured with synchrotron-based ultraviolet photoelectron spectroscopy (UPS). The LEED results for Au provide evidence for a lying down, striped phase from 2 L to 40 kL, a disordered, mixed phase up to ~2 ML, and a standing-up, @sr@3x@sr@3 R30° phase beyond ~2 ML of thiol dose. Vapor deposition on Ag results in a disordering of the surface, with a complete loss of the LEED pattern by ~5 kL. Ordered overlayer structures are observed on both the Pt(111) and Pt(100) surfaces at thiol doses below 1 L. For instance, a p(2x2) LEED pattern is observed at 0.1 L which transforms to a @sr@3x@sr@3 R30° pattern at ~25 L on the Pt(111) surface. Doses beyond ~2 L result in a disordered overlayer on this surface. The UPS spectra for solution growth SAMs on all three substrates are very similar. Four distinct peaks at 6.5, 10, 14, and 20 eV whose intensities are independent of the substrate are observed. The electronic structure of the vapor deposited films depends very strongly on the substrate. Weak thiol peaks are observed for coverages up to 100 kL on Au(111), consistent with the slow uptake observed with LEED. Emission features consistent with a fully saturated SAM are observed on Ag(111) for a dose of ~8 kL. Very weak thiol peaks are observed on the Pt surfaces for coverages up to 100 kL, which indicates that the uptake on Pt is slower than on Au. The ordered overlayer LEED patterns at low coverages, coupled with the very weak thiol features in UPS, point to a dissociative adsorption geometry for vapor deposition on Pt.

SS-TuP4 Comparison of Thiol and Disulfide Based Self-Assembled Monolayers (SAMs) by Reactive Ion Scattering Spectrometry (RISS), K.E. Joyce, University of Arizona; S. Ravindran, University of Texas; V.H. Wysocki, University of Arizona

Reactive Ion Scattering Spectrometry (RISS) was used to investigate self-assembled monolayers (SAMs) formed from symmetric disulfides and thiol solutions of corresponding chain lengths. A series of odd and even alkanethiol ((CH₂)₃(CH₂)₂)_nSH; n = 15, 16, 17) and disulfide ((CH₂)₃(CH₂)₂)_nS)₂; n = 15, 16, 17) SAMs were probed with benzene and pyrazine projectile ions to investigate both neutralization and reaction differences. RISS utilizes a tandem quadrupole mass spectrometer to select ions of a given mass-to-charge value and collides them with a given collision energy into the surface. Reactions of the ion beam with the surface are sensitive to factors such as the nature of the orientation of the terminal functional group. RISS revealed differences between disulfide and thiol based SAMs in both neutralization characteristics of the films, as evidenced by differences in total scattered ion currents, as well as differences in reactions via hydrogen and methyl abstractions from the surfaces. Systematic studies were conducted where fully formed disulfide based SAMs were introduced to thiol solutions to show incorporation of thiol species. FT-IR and contact angle experiments were also performed to examine SAM film chain-to-chain interactions.

SS-TuP5 The Impact of Molecular Properties on the Geometric Structure of Self Assembled Monolayers of Arenethiols on Cu(111), X. Lin, K.-Y. Kwon, K.L. Wong, L. Bartels, University of California at Riverside

Self assembled monolayers (SAMs) of organic molecules on metal surfaces are the subject of great interest due to their utility in nanodevices. The structure of individual SAMs is not only determined by the binding of their constituents to the substrate but also by intermolecular interactions. One challenging problem is to understand how molecule-molecule interactions affect the structure of the monolayer. We explored the impact of these interactions using thiophenol (TP) molecules on Cu(111) as a model system for aromatic thiol SAMs. Molecular properties can be changed in a systematic fashion by selective substitutions. We have performed STM studies of monolayers of thiophenol (TP) molecules and several halogen substituted para- and meta-X-TP derivatives (where X is Br, Cl or F). For both meta and para substituted molecules we find that the complexity of the monolayers increases with the electronegativity of the substituent, which suggests that electrostatic interactions of the molecular dipole and quadrupole moment play a critical role in determining the film structure. Penta-fluoro-substituted TPs exhibit no ordering at all, while unsubstituted TPs exhibit no long range order, yet are able to form stable aggregates up to seven molecules. Despite the fact that all the studied molecules share the common feature of having a thiol group as linker to the metal substrate, they display a vast diversity in their aggregation behavior as well as in their monolayer structures. This demonstrates the utility of this model system where the molecule-molecule interaction can be finely tuned to exhibit the full spectrum of aggregation behavior, from no ordering via clustering to formation of layers with complex patterns.

SS-TuP6 The Structure and Assembly of Ordered Alkanethiol Monolayers on GaAs (001), C.L. McGuinness, The Pennsylvania State University; D. Blasini, Cornell University; S. Uppili, The Pennsylvania State University; A. Shaporenko, M. Zharnikov, University of Heidelberg, Germany; D. Smligies, CHESS; D. Allara, The Pennsylvania State University

We demonstrate through glancing angle x-ray diffraction (GIXRD), near edge x-ray adsorption fine structure (NEXAFS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and contact angle measurements that alkanethiol molecules will form densely packed, translationally ordered monolayers on GaAs(001) by solution adsorption. GIXRD data show that the adlayer molecules form a hcp structure which is incommensurate with the underlying square lattice of the substrate, an indication of extensive reconstruction arising during chemisorption. The combination of IRS and NEXAFS data determine an average molecular axis tilt of 13-15° with a high average degree of conformational ordering of the chains. This work gives the first definitive evidence for translationally ordered monolayers on GaAs. The ability to make highly structured and stable molecular films on GaAs will be critical in applications including molecular devices and electron beam resists.

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SS-TuP7 Photoelectron Spectroscopy Studies of Potassium Deposition on Self-Assembled Monolayers, *H. Ahn, J.E. Whitten*, The University of Massachusetts Lowell

The deposition of potassium in ultrahigh vacuum on alkanethiols self-assembled on gold surfaces has been investigated with X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). Several issues have been studied, including extent of penetration of the metal and chemical interaction with the organic layer. In the case of methyl-terminated alkanethiols, it is found that potassium penetrates and interacts weakly with the monolayer, as indicated by minimal changes in the valence electronic spectra, even for large metal doses. Angle-resolved XPS and changes in the areas of the K2p, C1s, S2p, and Au4f peaks with increasing potassium dose confirm penetration. Work function measurements, obtained from the widths of the UPS spectra, are consistent with metal diffusion through the methyl-terminated alkanethiols to the gold interface, and work function changes approaching -2 eV are observed for several atomic layers worth of potassium. These types of studies have been performed for a variety of chain lengths and at cryogenic and room temperature. In general it has been found that potassium-induced C1s core level shifts, using XPS when the spectra are referenced to the Fermi level, are a misleading indicator of chemical interaction and essentially disappear when the peaks are referenced to the vacuum level. On the other hand, the Au4f peaks do not shift with respect to the Fermi level. These data suggest that the C1s alkanethiol orbitals are pinned to the vacuum level, and angle-resolved XPS has been used to quantify and study this effect as a function of depth.

SS-TuP8 Surface Nitridation of Terphenyl Methane Thiol Self-assembled Monolayer Using N@sub 2@ Neutral Beam Process, *Y. Ishikawa*, Tohoku University, Japan; *T. Ishida*, AIST, Japan; *S. Samukawa*, Tohoku University, Japan

To realize the future molecular scale devices, a fine surface modification method is quite important for controlling surface properties of organic molecules, such as the electric properties. Generally, the plasma processes were widely used to modify the surface for not only semiconductor devices but also polymer surface. However, for the surface modification of organic monolayers that can be utilize molecular scale device, the plasma processes cannot be used because of radiation of VUV, UV photons and charged particles from plasma to surface. Namely, the organic monolayers are considered to be broken due to radiation of these particles. To eliminate these radiation damages, we have already proposed the neutral beam process.^{1,2} This process could perfectly prevent the charged particles and ultraviolet photons to the surface and only the low energy neutral beam (accelerated atom and molecular beam) were irradiated to the substrates. In this paper, the pulse-time-modulated (TM) N@sub 2@ beam irradiation¹ was investigated to control the surface nitridation of terphenyl methane thiol self-assembled monolayer (TP1-SAM).^{3,4} The N@sub 2@ neutral beam irradiation was modulated at a few tens microseconds to control the degree of surface nitridation. By using the novel modification method, we investigated the surface nitridation of TP1-SAM with maintaining the bulk structure. After the beam irradiation, we evaluated the amount of surface nitridation using the x-ray photoelectron spectroscopy. We found that the TM N@sub 2@ beam could precisely control the surface nitridation of TP1-SAM by changing the beam modulation period. ¹ Samukawa et al.: *J. Vac. Sci. Tech.*, A22, 245 (2004) ² Y. Ishikawa et al.: AVS 51st international symposium, PS+BI-FrM9 (2004) ³ T. Ishida et al.: *Langmuir*, 18, 83 (2002) ⁴ T. Ishida et al., *Langmuir*, 18, 10499 (2002).

SS-TuP10 Reaction Site Selectivity of Analyte Gases on Metallophthalocyanines: A Density Functional Theory Study, *N.L. Tran, S.R. Bishop, G.C. Poon, A.C. Kummel*, University of California at San Diego

Numerous studies have reported the use of metallophthalocyanines (MPcs) as thin film sensors for analyte gases, but a basic understanding of gas chemisorption onto these metal coordination complexes is lacking. Density functional theory was used to investigate the mechanism of chemisorption of two different analytes, NO and NH@sub 3@, onto two different MPcs, CoPc and FePc. Four analyte binding sites on the MPcs were investigated: (i) metal centers, (ii) inner ring nitrogen atoms, (iii) outer ring nitrogen atoms, and (iv) organic rings. For NO on FePc and CoPc, simulations show chemisorption onto the metal centers and physisorption onto the outer ring nitrogens and organic rings. In contrast, NH@sub 3@ chemisorbs onto the FePc metal center and physisorbs onto the Co metal. All other binding sites were not energetically favorable. Additionally, these calculations show a multi-step absorption mechanism in which NO initially binds to the inner

ring nitrogens and then undergoes a barrierless migration to the deep chemisorption well on the metal centers for FePc and CoPc. PDOS simulations reveal that the binding of NO and NH@sub 3@ to the FePc metal center significantly alters the electronic structure of the clean FePc. However the two systems have opposite charge transfer mechanisms: charge is accepted by the NO chemisorbate from the Iron metal but is donated from the NH@sub 3@ chemisorbate to the Iron metal. These different charge transfer mechanisms will differentially affect charge relaxation times and the photoconductivity threshold in an MPc film and therefore can be used to identify analytes instead of just measuring analyte concentration. Additionally, simulations are being performed to study the possibility of subsurface diffusion of the NO molecule into the bulk.

SS-TuP11 Thermochromism Effects in Poly(3-hexylthiophene), *D.Q. Feng*, University of Nebraska-Lincoln; *P.A. Dowben*, University of Nebraska-Lincoln, US

We find evidence for a gradual semiconductor to insulator transition in poly(3-hexylthiophene), that appears to be mediated by a low density of defects states within the highest occupied molecular orbital to lowest unoccupied molecular orbital gap. The photoemission and transport measurements indicate that a loss of charge mobility occurs with decreasing temperature, while the molecular configuration also changes with temperature. Defects states have been identified in photoemission and these defects states are believed to be very heterogeneous.

SS-TuP12 Adsorption and Decomposition of Triethylsilane on Si(100), *J. Lozano, D. Early, L. Bockewitz, J.H. Craig, Jr., P.W. Wang, K.R. Kimberlin*, Bradley University

The adsorption and decomposition of triethylsilane (TES) on Si(100) were studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and x-ray photoelectron spectroscopy (XPS). Si(100) samples were dosed with TES at 100K. Desorption of mass 27 (attributed to ethylene) takes place at 750K, followed by desorption of hydrogen at 815K. This is indicative of a ???-hydride elimination process that results in at least partial removal of carbon species from the surface. At multilayer coverages, physisorbed species accumulate on the surface, as indicated by a low temperature desorption peak at 170K. At the highest TES exposures (~10L), a second low temperature TPD peak appears at 280K. This suggests that the second-layer physisorbed state is slightly more tightly bound than multilayer TES. In order to confirm this, HREELS and XPS data were obtained immediately following sequential thermal anneals to increasing temperatures, which were determined by landmark features in the TPD spectra. A model of the thermal evolution of TES on Si(100) based on the results obtained will be presented.

SS-TuP13 Low Temperature Decomposition of Triethylsilane on Si(100) by Electron Irradiation, *J. Lozano, D. Early, L. Bockewitz, P. Petrany, J.H. Craig, Jr., P.W. Wang, K.R. Kimberlin*, Bradley University

Electron-induced decomposition of triethylsilane (TES) on Si(100) at 100K was studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), electron stimulated desorption (ESD), and x-ray photoelectron spectroscopy (XPS). Si(100) samples were dosed with TES and then irradiated with 600-eV electrons for 5 minutes. During electron irradiation, ESD of neutral particles was monitored. Only a small hydrogen ESD signal was detected at all TES coverages. Following electron irradiation of multilayer TES/Si(100), TPD data exhibited decreased desorption of physisorbed species and a dramatic increase in mass 2, 27, and 59 desorption, compared to TPD from un-irradiated surfaces. This indicates that electron irradiation resulted in decomposition of TES and deposition of large fragments on the surface. Fragmentation of TES by electron irradiation was studied by obtaining HREELS and XPS data following sequential thermal anneals of the electron-irradiated surface to increasing temperatures.

SS-TuP14 Molecular View of the Selforganization Processes on Silicon: Experimental and Computational Studies of Nitrobenzene and Hexafluoroacetylacetone on Si(100)-2x1, *L.P. Méndez De Leo, L. Pirolli, A.V. Teplyakov*, University of Delaware

Molecular selforganization on semiconductor surfaces bears a variety of future applications: from deposition processes to molecular electronics. Here we present two different reactions on Si(100)-2x1 surface studied by an array of surface analytical techniques and by computational methods. The reaction of nitrobenzene on Si(100) surface is a prototypical model reaction for understanding the interaction of bifunctional molecules with the surface and for directing self-organization processes at cryogenic

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temperatures. The preferred reaction of the nitro-group has been studied previously and, along with the exceptional thermal stability of the resulting monolayer, provides an opportunity to manipulate surface reactions that have a long list of possible pathways. Computational analysis together with the vibrational studies suggest that only a few types of surface bonding are possible in this reaction and the interaction between the neighboring chemisorbed nitrobenzenes lay a groundwork for studies of electron transfer processes involving the σ - π interaction of the phenyl groups. Hexafluoroacetylacetone (hfac) is a common ligand in chemical vapor deposition processes of copper. The interaction of this ligand with the Si(100)-2x1 surface is of paramount importance for the deposition processes, at the same time, it possesses several functionalities and the utilization of the preferential binding of these functional groups to the surface can be used in the future not only to modify the interactions of the organometallic precursors with the substrate but also to understand the general rules in functionalization of the surface with complex multifunctional molecules. Just like in the case of nitrobenzene, computational methods were used in conjunction with the experimental studies to elucidate the mechanism of hfac interaction with Si(100)-2x1.

SS-TuP16 Adsorption and Dissociation Studies of Tri-ethylgermane on the Si(100) Surface. A. Brickman, P. Petrány, J. Lozano, J.H. Craig, Jr., P.W. Wang, Bradley University

Adsorption of tri-ethylgermane (TEG) on the Si(100) surface has been studied using temperature programmed desorption (TPD), electron stimulated desorption (ESD) in a time-of-flight mode, and high resolution energy loss spectroscopy (HREELS). Evidence for a beta-hydrogen elimination process will be presented in desorption spectra. Electron driven dissociation effects on the adsorbed TEG layer will be presented. The extent to which germanium is deposited on the Si(100) surface subsequent to TEG dissociation will also be discussed as characterized by X-ray photoelectron spectroscopy (XPS).

SS-TuP17 The Adsorption Structure of Histidine on Ge(100). S.J. Jung, S. Kim, Korea Advanced Institute of Science and Technology (KAIST), Korea; S. Hong, Sejong University, Korea

The adsorption of histidine molecule on the Ge(100)-2x1 surface was investigated using both scanning tunneling microscopy (STM) and the density functional calculation. Various adsorption features of histidine are founded to be formed under different conditions of temperatures and coverages. When histidine is exposed to a clean Ge(100) surface at 300 K, the histidine appears as round shaped bright protrusion in STM image, which is randomly distributed over the surface. After annealing the surface at 380 K, we found a short range ordering in molecular rows. When histidine is deposited onto Ge (100) at 380 K, histidine is found to form dumbbell shape protrusions that are located in either parallel or vertical direction to the dimer row. At the saturation coverage ($\theta = 0.25$ ML), however, the STM image show globally ordered array consisted of dumbbell shape features without regard to the direction of dimer row of the Ge (100) surface. Such global ordering implies that the interaction between histidine molecules is much more significant than the interaction between the molecules and the surface dimer. The ab initio calculation also suggests that the surface at saturation coverage has an additional stability, induced by the lateral interaction, compared to that at low coverage. Based on the STM results and ab initio calculation, we will present the adsorption structures, inter-molecular interaction and ordering of histidine molecules on the Ge(100) surface.

SS-TuP18 Chiral Attachment of Styrene Mediated by Surface Dimers on Ge(100). Y.J. Hwang, Korea Advanced Institute of Science and Technology (KAIST), South Korea; A. Kim, Korea Advanced Institute of Science and Technology (KAIST), South Korea, Korea; E.K. Hwang, S. Kim, Korea Advanced Institute of Science and Technology (KAIST), South Korea

We determine the absolute chirality of adsorbed styrene using scanning tunneling microscope (STM) and demonstrate a novel method for the achiral molecule to produce dimeric enantiomers and diastereomers covalently bonded to the Ge(100) surface. On the Ge(100) surface, styrene adsorbs in a paired end-bridge between two neighboring Ge dimers within the same dimer row (PEB) as well as on the top of a single Ge-Ge dimer (OT). The OT configuration is classified into (S) and (R) OT chiral products according to the direction in which styrene molecule attacks the Ge dimer. Similarly, in case of paired adsorption, we found enantiomeric (R,R)- and (S,S)-trans-PEB and diastereomeric (R,S)-cis-PEB configurations through STM images. Temperature programmed desorption (TPD) spectra indicated that the desorption temperatures for the OT and PEB configurations are 320 K and 365 K, respectively. STM measurements

indicate that the OT configurations is converted into the thermodynamically more stable PEB configurations either by annealing a styrene-adsorbed Ge surface at 340 K or by scanning the Ge surface at high bias voltages. Such conversion of chiral configurations suggests the possibility of the controlled adsorption of chiral molecules on the surface. Therefore, we anticipate that the chiral structures prepared by paired adsorption will provide chiral organic hybrid systems on semiconductor surfaces for potential application to semiconductor-based molecular devices, chiral sensors, and heterogeneous enantioselective catalysis. @FootnoteText@ @footnote 1@ Hwang, Y. J.; Kim, A.; Hwang, E.; Kim, S. J. AM. CHEM. SOC. 2005, 127, 5016-5017

SS-TuP19 Phonon-Activated Electron-Stimulated Desorption of Halogens from Si(100)-(2x1). B.R. Trenhaile, V.N. Antonov, G.J. Xu, A. Agrawal, A.W. Signor, R.E. Butera, K.S. Nakayama, J.H. Weaver, University of Illinois at Urbana-Champaign

Spontaneous desorption of Cl, Br, and I from n- and p-type Si(100)-(2x1) was studied with scanning tunneling microscopy at temperatures of 620 \pm 825 K where conventional thermal bond breaking should be negligible. The activation energies and prefactors determined from Arrhenius plots indicate a novel reaction pathway that is initiated by the capture of electrons that have been excited by phonon processes into Si-halogen antibonding states. This configuration is on a repulsive potential energy surface, and it is sufficiently long-lived that desorption occurs, as in electron-stimulated-desorption. Surprisingly, the desorption rates for differently doped samples crossed and, above a critical temperature, the reaction with the largest activation energy had the highest rate. This is explained by large entropy changes associated with the multiphonon nature of the electronic excitation. For Cl desorption from p-type Si, these entropy changes amounted to 34 kB. They were 19 kB, 13 kB, and 8 kB for Br desorption from p-type, lightly-doped n-type, and heavily-doped n-type Si, respectively. The desorption rates for I were nearly three orders of magnitude larger than the rates observed for Cl and Br. Here, the Si-I antibonding states overlap the conduction band minimum, and we propose that electrons impinging on the surface with this energy can be captured by the Si-I antibonding states. Together, these results reveal that a complex relationship exists between phonons and electronic excitations during chemical reactions at surfaces.

SS-TuP20 Water Etching of Hydrogen-Terminated Si(100): Implications for Oxidation. S.K. Green, Smith College; M.F. Faggin, M.A. Hines, Cornell University; K.T. Queeney, Smith College

While it has been known for some time that deoxygenated H₂O will etch hydrogen-terminated Si(100), our recent work shows that this etching generates a surface of surprising homogeneity. Transmission infrared spectroscopy is used both to examine the mechanism of this etching process and to decipher the surface termination of the structures formed. Analysis of both the stretching and bending modes of SiH_x species reveals characteristic {100} and {111} facets that can be related to structures formed on extended (100) and (111) surfaces. Selective isotopic labeling reveals that the initial, H-terminated surface is completely removed within 10 minutes' immersion in room-temperature, deoxygenated H₂O. The rate of this reaction is therefore fast compared to the rate of oxidation of H:Si(100) by O₂(aq) that is normally present in air-equilibrated H₂O, making the etching process a critical factor in the oxidation of Si(100) in neutral or basic aqueous solutions.

SS-TuP21 Substrate-Bias-Dependent Orientation-Selective-Epitaxial Growth of CeO₂ Thin Films on Si(100) Substrates by Magnetron Reactive Sputtering. T. Inoue, Iwaki Meisei University, Japan; D. Kukuruzyak, T. Chikyo, National Institute for Materials Science, Japan; K. Kato, Fukushima Technology Centre, Japan

Although many reports have been made on the growth of CeO₂(110)/Si(100), orientation selective epitaxial (OSE) growth of CeO₂(100) and CeO₂(110) layers is found to be capable by controlling substrate bias and plasma power in reactive dc magnetron sputtering enhanced with an inductively coupled rf plasma. We adopted two step growth method; ultrathin metallic Ce layer deposition at room temperature using Ce metal target followed by silicidation process at several hundreds degree C, and subsequent reactive sputtering in an Ar/O₂ mixture environment at elevated temperature. Reactive magnetron sputtering is performed at rf power of 50 W for induction coil and 120 W for cathode dc plasma power under substrate bias ranging between -25 and +25 V varied by 5~V step. Growth rate is controlled in between 0.2 and 0.4 nm/s varying Ar gas flow between

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4 and 15 sccm. Oxygen gas flow for reactive sputtering is 1 sccm. CeO@sub 2@(100) layers grow under substrate bias around both +15 and -15 V with a width of approximately 10 V, otherwise CeO@sub 2@(110) layers grow. The orientation selection is found to be also dependent on plasma power, in other words the growth rate: upper limit in growth rate exists for (100) layer growth, above which (110) layer grow. Precise mapping of growth parameters for OSE, in terms of substrate bias and growth rate, for the growth of CeO@sub 2@(100) films are attained from a lot of growth experiments. In order to get insight into orientation selectivity depending on substrate bias, we are making systematic experiments to study orientation component changes with substrate bias in CeO@sub 2@ layers, which leads to a clue for understanding the relation between orientation of nuclei and substrate bias. We also demonstrate the experimental results indicating effectiveness of assistance by oxygen radical beams on reactive sputtering; successful epitaxial temperature lowering and crystalline quality improvements. Characterization of the epitaxial films are carried out using RHEED, XRD, XTEM and AFM. This orientation selective epitaxial growth (OSE) technology will be useful for sophisticated structure using multiple layer epitaxy. @FootnoteText@ @footnote 1@ T. Inoue et al., J. Vac. Sci. Technol. A 22(1), 46 (2004).

SS-TuP22 Measurement of Surface States Above the Valence Band Maximum in n-type GaN(0001) Using Angle-Resolved Photoemission Spectroscopy, L. Plucinski, L. Colakerol, S. Bernardis, Y. Zhang, K.E. Smith, I. Friel, T.D. Moustakas, Boston University

We have performed a high resolution angle-resolved photoemission study of N-polar GaN(000-1).@footnote 1@ We have observed sharp dispersive surface states extending approximately 2 eV above the valence band maximum (VBM). These states agree with those predicted for a N-polar GaN(000-1) 1x1 reconstructed surface. Samples were grown by plasma-assisted molecular beam epitaxy on c-plane sapphire. They were doped with Si and the free-carrier concentration was 3×10^{18} cm⁻³ which resulted in a slightly degenerate n-type material at room temperature. Experiments were performed at the U5UA undulator beamline at the NSLS, using a Scienta SES100 electron energy analyzer. Clean surfaces were prepared in situ by sputtering with nitrogen ions and annealing in UHV. Samples were held at 120 K when recording spectra. We have found a full width at half maximum for the surface state feature of 400 meV at K-point of surface Brillouin zone. The width is limited by surface imperfections and the existence of reconstructions on the surface other than a simple 1x1. Our results are similar to those obtained for p-type GaN.@footnote 2@ However, in case of p-type GaN the surface likely contained 30 degree rotated domains.@footnote 3@ We show that in the case of n-type GaN the surface is free of domains. @FootnoteText@ @footnote 1@ Supported in part by the NSF DMR-0311792, by U.S. ARO 40126-PH, and by U.S. AFOSR. Our spectrometer system is funded by U.S. ARO DAAD19-01-1-0364. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ P. Ryan, Y. C. Chao, J. Downes, C. McGuinness, K. E. Smith, A. V. Sampath, and T. D. Moustakas, Surf. Sci. 467, L827 (2000).@footnote 3@ F.-H. Wang, P. Krueger, and J. Pollmann, Surf. Sci. 499, 193 (2002).

SS-TuP23 Step Edge Diffusion in Strained Compound Semiconductors, C. Pearson, University of Michigan-Flint; J. Mirecki Millunchick, University of Michigan

Understanding the growth of strained alloys films is an enduring problem in surface science. Models of strained film growth based on elastic strain energy predict unique morphologies for different strain: islands upon large terraces for compressive films and mesas separated by trenches for tensile films. Using a combined MBE-STM system, we have imaged 2 ML thick films both in compression (InAs or GaSb) and in tension (GaAs or AlAs) grown on InP(001) near T=480°C using a group III growth rate of ~0.2 ML/s with an approximate group V/III ratio of 5. A roughness analysis reveals that the skewness of the height distribution for InAs is positive, which is indicative of a morphology dominated by islands while for AlAs the skewness is negative, which is indicative of a morphology dominated by holes. These results agree with the previously described morphologies predicted using elastic strain energy considerations. The Ga containing compounds also follow this strain energy trend, except the terraces or mesas have significantly rougher steps and higher surface anisotropies. These observations suggest that in addition to the sign of the misfit strain, factors such as step edge diffusion contribute to surface roughness. From an analysis of the images we compute the step edge density (step edge length per unit area) versus deposition flux and use a recent level set model@footnote 1@ to extract values of step edge diffusion. These results

may explain the variety of microstructures observed in short period superlattice structures of these compounds that exhibit lateral composition modulation. @FootnoteText@ @footnote 1@ C. Ratsch, J. Garcia, and R. E. Caflich, submitted to Applied Physics Letters.

SS-TuP24 Comparative Study of the Initial Oxidation Kinetics on Si(001) and Ti(0001) Surfaces by Real-Time Ultraviolet Photoelectron Spectroscopy, Y. Takakuwa, S. Ogawa, M. Ohira, IMRAM, Tohoku University, Japan; Y. Mizuno, Stanford University

Oxidation on Si and Ti surfaces leads to growth of SiO@sub 2@ and TiO@sub 2@ layer, respectively. In order to clarify the behavior of adsorbed oxygen during growth of oxide, the initial oxidation kinetics on Si(001)2x1 and Ti(0001)1x1 surfaces was comparatively investigated by real-time ultraviolet photoelectron spectroscopy to measure the oxygen uptake and work function @phi@ simultaneously. On the Si surface at 357°C, the @phi@ increases gradually with increase of O@sub 2@ dosage after showing a dip due to negative charges, while the dip disappears with elevating temperature. The negative change of @phi@ means diffusion of adsorbed oxygen into the subsurface. On the other hand, a dip in @phi@ appears at temperatures above 300°C on the Ti surface. This suggests that adsorbed oxygen on the Ti surface can easily diffuse into the subsurface when elevating temperature, although such diffusion of adsorbed oxygen tends to occur on the Si surface when lowering temperature. The difference of adsorbed oxygen behavior between Si and Ti surfaces is discussed in terms of the O@sub 2@ dissociative adsorption kinetics and crystallographic nature of oxide, amorphous SiO@sub 2@ and crystalline TiO@sub 2@.

SS-TuP25 Stress-induced Transformation between Si(5 5 12)-2x1 and Si(7 7 17)-2x1, S. Cho, J.M. Seo, Chonbuk National University, Korea

From the reconstructed Si(5 5 12)-2x1, the area of locally-converted Si(7 7 17)-2x1 has been detected by scanning tunneling microscopy(STM). The atomic structure of Si(7 7 17)-2x1 has turned out to be the same as that of Si(5 5 12)-2x1 with missing one of (337) sections, namely D(337) with a dimer-facing-adatom(D/A) row. In this structural transformation from (5 5 12) to (7 7 17), neither the number of atoms nor the dangling-bond number changes, but the surface atoms simply rebond under the external stress originating from the (113) facet parallel to 1-D row. By the distribution of (7 7 17) domain, the direction and size of compressive surface-stress on Si(5 5 12)-2x1 can be deduced, implying that (7 7 17) can be utilized as a stress-indicator of nanometer scale on (5 5 12).

SS-TuP26 Thermal Stability of Nickel Silicide Layer on Si, Relaxed-SiGe/Si, Strained-Si/relaxed-SiGe/Si Heterostructure, J.H. Ko, C.H. Jang, Sungkyunkwan University, Korea; S.H. Kim, Y.-J. Song, Electronics and Telecommunications Research Institute, Korea; N.-E. Lee, Sungkyunkwan University, Korea

MOSFET device utilizing a strained-Si channel on relaxed SiGe buffer layer is one of the most promising structure for the next-generation CMOS integration scheme below 50 nm technology node because of its high channel mobilities compared to bulk Si and compatibility with conventional Si CMOS processes. Rapid thermal annealing was performed at 400 °C and then post thermal annealing was performed at of 600~800 °C as following process. Nickel silicide was formed on strained-Si/relaxed-SiGe/Si (001) and relaxed-SiGe/Si (001) and Si (001) using a sacrificial strained-Si layer and its morphological characteristics were investigated. Nickel silicide layers were grown by rapid thermal annealing of the samples with the structure of Ni (10.92 nm)/strained-Si (20 nm)/relaxed-SiGe/Si (001) at the annealing temperature (TA) range of 400~800 °C. And we deposited Ni at each 11nm and 21nm to know what is different. When we deposited 11nm Ni that it's interface roughness very bad but 21nm Ni deposited whose interface roughness improved. The phase formation, surface and interfacial morphologies, and electrical properties of the resulting sample were characterized by various measurement technique, including X-ray diffraction, scanning electron microscopy, cross-sectional transmission electron microscopy and the four-point probe method. As the result when we measured sheet resistance Ni 11 nm on strained-Si/relaxed-SiGe/Si (001) and relaxed-SiGe/Si (001) and Si (001) it were determined to be 9.778, 11.083, 8.464 @ohm@/sq. at 400 °C and it were determined 4.428, 5.453, 4.715 @ohm@/sq. at 400 °C 21 nm. Sheet resistance were determined 160.98, 78.79, 138.633 and 92.397, 65.857, 146.875 @ohm@/sq. at 800 °C 11nm and 800 °C 21 nm, respectively

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SS-TuP27 Lithium Hydride and Lithium Amide for Hydrogen Storage, J. Engbaek, Technical University of Denmark, Denmark; **G. Nielsen,** Technical University of Denmark; **I. Chorkendorff,** Technical University of Denmark, Denmark

Hydrogen storage is a serious showstopper for using hydrogen in the transport sector therefore this field has gained renewed interest. Lithium amide has a high hydrogen storage capability; 10.4wt.% hydrogen. In this study surface reactions of thin films of lithium with hydrogen and ammonia is studied under well controlled conditions with pure hydrogen and ammonia in a UHV-chamber. Thin well-characterized Lithium films from sub monolayer to several monolayers were grown on a nickel(111). The films of pure lithium and films reacted with hydrogen and ammonia were characterized with Auger, TPD and LEED. From the LEED patterns we have found that one monolayer of pure lithium form a stable 4x4 reconstructed surface with a coverage of 3 Li atoms to 4 Ni atoms. Lithium hydride was made by exposing a pure lithium film utilizing an atomic hydrogen source. TPD experiments were used to investigate the stability of the lithium / lithium hydride films and surprisingly we have found that lithium evaporate before lithium hydride. Similarly the stability of the lithium hydride / lithium amide was investigated by evaporating Lithium in an atmosphere of ammonia to make thin films of lithium amide. TPD experiments showed that lithium amide decompose at an even higher temperature than lithium hydride and lithium. This significantly complicates the use of lithium amide powder as a hydrogen storage system. The results made under UHV are compared to experiments on ball milled lithium hydride and lithium amide powders.

SS-TuP28 Photoemission and Secondary Ion Mass Spectrometry Study of Uranium Passivation by Ion Implantation, A.J. Nelson, T.E. Felter, K.J. Wu, C. Evans, J.L. Ferreira, W.J. Siekhaus, W. McLean, Lawrence Livermore National Laboratory

Implantation of C⁺ ions into U²³⁸⁺ produces a physically and chemically modified surface layer that prevents further air oxidation and corrosion. X-ray photoelectron spectroscopy and secondary ion mass spectrometry were used to investigate the surface chemistry and electronic structure of this C⁺ ion implanted polycrystalline uranium compared to an unimplanted region of the sample, both regions exposed to air for more than a year. In addition, scanning electron microscopy was used to examine and compare the surface morphology of the two regions. High-resolution U 4f, O 1s and C 1s core-level and valence band spectra clearly indicate carbide formation in the modified surface layer. The time-of-flight secondary ion mass spectrometry depth profiling results reveal an approximately 200 nm thick UC layer with little or no residual oxidation at the carbide layer/U metal interface and a small amount of oxidation at the surface. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

SS-TuP29 Surface Chemistry at a LiF-BeF Molten Salt / Beryllium Metal Interface: Probing the Structure and Composition of the Post-Reaction Interface with Microscopy and Electron Spectroscopy, P.J. Pinhero, G.R. Smolik, M.F. Simpson, R.A. Anderl, J.P. Sharpe, D.A. Petti, Idaho National Laboratory

Molten FLiBe (2LiF:BeF₂) is a candidate as a cooling and tritium breeding media for future fusion power plants. Neutron interactions with this salt will produce tritium and excess free fluorine ions. Beryllium metal has been demonstrated as an effective REDOX control agent to prevent the free fluorine from reacting with structural metal components. Simply-designed experiments were performed to measure the extent and rate of Be solubility in a FLiBe mixture that was continuously supplied with HF. This paper presents results from post-test examination of the reacted surfaces. This information provides a good link to understanding the reactions taking place at the interface between the molten salt solution and the Be rod. Potential influences of bi-metal exposures, some with direct coupling, e.g., Be to Ni and Be to Fe were examined. The impacts of the bi-metal contacts upon Be dissolution in the FLiBe and potential alloying with the transition metals are examined using scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning Auger microscopy (SAM), and x-ray photoelectron spectroscopy (XPS).

SS-TuP30 Tuneable Rough Surfaces: A New Approach for Elaboration of Superhydrophobic Films, L.M. Lacroix, M. Lejeune, L. Ceriotti, M. Kormunda, T. Meziani, P. Colpo, F. Rossi, Joint Research Centre Ispra, European Commission, Italy

The hydrophobic and repelling solid surfaces have found a large utility on our daily lives. The present work describes the process enabling the

production of superhydrophobic surfaces by tailoring their surface topography and chemical properties. These surfaces have been developed using a simple plasma based techniques combining plasma etching and plasma polymerization on silicon substrates. These techniques have been chosen because they provide features such as large area processing and high reproducibility. The key step of this process is the modification of the surface topography of the substrate to create high roughness before deposition of fluorocarbon coating. The roughness on silicon wafer is induced by the over-etching of a photoresist layer by a SF₆ plasma treatment. The different layers obtained exhibit contact angles from 102 up to 180 depending of the preparation conditions. The observations of the topology by scanning electron microscopy reveal that the presence of dendrites on the surface of the substrate favors the superhydrophobicity of the films. The variations of the contact angle have been explained using the Wenzel's or Cassie's models.

SS-TuP31 Friction Force Microscopy on Monolayer NaCl Films, P. Delage, T. Filleter, S. Maier, R. Bennewitz, McGill University, Canada

Friction and wear on metal surface can be greatly reduced by solid lubricant layers. We have performed Friction Force Microscopy on a model system, ultra-thin films of NaCl on a Cu(100) substrate, in order to study the microscopic mechanisms of friction in solid lubricant films. The NaCl films were grown by means of molecular evaporation in ultra-high vacuum conditions. Large islands of monolayer films are covered with nanometer-scale rectangular islands forming the subsequent layers. The decay of island density close to the edge of the film suggests a low barrier for NaCl molecules diffusing from the first monolayer to the copper substrate. In regions where the film grows over substrate terraces, island density increases while islands size decreases. Stable friction experiments were possible even on single monolayers of NaCl, and atomic stick-slip processes have been recorded.

SS-TuP32 Single Asperity Atomic Force Microscope Studies of the Chemical Mechanical Planarization of Silicate Glasses@footnote 1@, F. Stevens, S.C. Langford, J.T. Dickinson, Washington State University

The Atomic Force Microscope (AFM) is not only an imaging tool, but also can be employed to apply highly localized stresses to a surface. In the presence of liquids, we can investigate a number of tribochemical processes. Here we present the results of fundamental studies of the simultaneous application of chemical agents and mechanical stress to amorphous sodium trisilicate. We show the consequences of combining highly localized mechanical stress (due to contact with the AFM tip) with exposure to aqueous solutions of known pH. This experiment incorporates many features of single-particle/substrate/slurry interactions in Chemical Mechanical Planarization (CMP). Importantly, we show quantitative, correlated data on the wear of both the AFM tip and the glass substrate. The significant modification of the tip during a single wear experiment has profound effects on the rate of material removal from the exposed surface. Such measurements allow us to determine how substrate wear depends on the stress applied by the tip. In addition, the temperature of the solution and substrate can be changed over a limited range. We examine solid surfaces of silicate glasses, inorganic single crystals, and silicon nitride. Quantitative models are presented to account for the observed nanometer-scale surface modification. @FootnoteText@ @footnote 1@This work was supported by the National Science Foundation.

SS-TuP33 Non Contact Polishing Technique for Metal Foils, C.C. Chang, Industrial Technology Research Institute, Taiwan, R.O.C., Taiwan; **C.J. Wu,** Industrial Technology Research Institute, Taiwan, R.O.C.

Non-contact polishing technique for surface treatment of metal foils has been studied. This paper presents a successful electropolishing technique to deal with the surface of stainless steel foils. This technique is capable of polishing large area(over 200mm width),ultra thin(below 50µm thick) metal foils to be with electric grade surface(Ra<0.02µm), and potential for mass production. The metal foils with electric grade surface could be used of a substrate of flexible electronic devices.

Electronic Materials and Processing Room 309 - Session EM+SS-WeM

Contacts to Organic and Molecular Devices

Moderator: Y. Roichman, Princeton University

8:20am **EM+SS-WeM1 Energy Level Alignment at Interfaces in Organic Semiconductor Devices**, *K. Demirkan, A. Mathew, S. Vaidyanathan, Z.I. Niazimbetova, H. Christian-Pandya, M.E. Galvin, R.L. Opila*, University of Delaware

Poly-phenylene vinylene based organic semiconductor polymers and oligomers were studied using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron spectroscopy (UPS). Valence bands and highest occupied molecular orbitals (HOMOs) (with respect to Fermi level) for these organic structures were determined. Due to the high electron withdrawing property of the oxadiazole moiety, polymers, which have a higher oxadiazole density, are found to have lower energy levels. Using optical absorbance spectra, the lowest unoccupied molecular orbitals (LUMO) for some of the organic semiconductor materials were estimated and the basic energy level diagrams were established with respect to the underlying electrode. The valence band spectra of the polymers spin coated on different substrates did not show any substantial variation except for shifts in the entire spectra. In the Mott-Schottky limit, the energy difference between the electrode Fermi level and the HOMO of the organic layer is expected to follow the work function of the electrode. The interface slope parameter, a measure of the change in HOMO-Fermi level difference as a function of electrode work function, was found to vary between 0.4 and 0.9. These values are intermediate to Mott-Schottky and Fermi level pinning. We will explain the interface slope parameter in light of the interfacial dipole and charge neutrality level at organic/metal interfaces.

8:40am **EM+SS-WeM2 Towards Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces**, *C. Zhou, G. Nagy, A.V. Walker*, Washington University in St. Louis

We have developed a robust method by which to construct complex two- and three- dimensional structures based on controlling surface chemistry. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Our method is extensible to many different types of materials, easily parallelized, affords precise nanoscale placement and is fully compatible with photolithographic fabrication processes. The method is based on the deposition of metals on UV-photopatterned self-assembled monolayers (SAMs). To demonstrate the method we have selectively vapor-deposited Mg on a patterned -CH₂sub 3@/-COOH terminated alkanethiolate surface. The deposited metal penetrates through the -CH₂sub 3@ SAM to the Au/S interface while reacting with the -COOH terminal group and accumulating on top of the other SAM.

9:00am **EM+SS-WeM3 Interface Disorder and Charge Injection into Organic Semiconductors**, *M.A. Baldo, B.N. Limketkai*, MIT **INVITED**

In this talk, we examine the effect of structural disorder at the injection interface on the current-voltage (IV) characteristics of organic semiconductors. We find that structural disorder at the injection interface creates energetic disorder, which in turn may dominate the IV characteristics of these materials. We will describe the effects of interfacial disorder on charge injection in several model systems: flat metal electrodes, rough metal electrodes, and highly conductive polymer electrodes. Disorder is most important at interfaces with relatively small energetic barriers between the metal and semiconductor.

9:40am **EM+SS-WeM5 Modelling Inhomogeneities of Organic Device Contacts: Organic Film Growth on Nanostructured Surfaces**, *M.G. Ramsey, B. Winter, S. Surnev, G. Koller, F.P. Netzer*, Karl-Franzens-University Graz, Austria

In this contribution the growth, geometric and electronic structure of sexiphenyl films grown on clean Cu(110) and mesoscopically patterned Cu(110)-(2x1)O will be presented. The results highlight the effects of the atomic and nanometric substrate structure on the growth and electronic level alignment of active organic films. Scanning tunnelling microscopy (STM) reveals that on the clean Cu the molecules align parallel to each other and are highly mobile in one surface direction. By monolayer coverages a complete layer forms reminiscent of a smectic liquid crystal phase. Despite the lack of strict long range order the molecules align in

strings with a periodicity determined by intermolecular interactions, while the periodicity between the strings is determined by the substrate periodicity. In contrast when the substrate is covered with a half monolayer of oxygen the molecules appear not to wet the surface and, apart from at defects, are not visible in STM. On the mesoscopically patterned Cu(110)-(2x1)O (stripes of clean and oxygen covered surface with a periodicity of ~ 7 nm) the molecules first appear at the Cu-CuO boundaries and then grow preferentially on the clean Cu stripes. Growth and electronic structure on the three basic substrate situations are also followed by angle resolved ultraviolet photoemission spectroscopy (ARUPS). These results highlight the problems of imaging such wide band gap materials with STM and indicate that the 6P does in fact wet the Cu(110)-(2x1)O and that the visibility of the molecule is dependent on charge transfer states in the gap. These ARUPS results will also be discussed in terms of the electronic level alignment on inhomogeneous surfaces where large band offsets between molecules on different regions occur.

10:00am **EM+SS-WeM6 The Influence of Alkyl Side-chains and Charge-Transfer Complex Formation on Sexithiophene/Metal Interface Energetics**, *S. Duhm, H. Glowatzki*, HU-Berlin, Germany; *R.L. Johnson*, Hamburg University, Germany; *J.P. Rabe, N. Koch*, HU-Berlin, Germany

The energy level alignment at metal/organic interfaces is a key issue for improved performance of novel organic (opto-) electronic devices. In certain cases, solution-based processing of organic materials (i.e., spin-coating, ink-jet printing) is preferred over vacuum sublimation. Frequently, alkyl side-chains are attached to the conjugated moieties for improved solubility. In order to investigate the influence of alkyl side-chain addition on interface energetics, we studied interfaces formed between the organic molecules sexithiophene (6T) and @alpha@.@omega@dihexylsexithiophene (DH6T) and the metal surfaces Ag(111) and polycrystalline Au with ultraviolet photoelectron spectroscopy (UPS). Samples were prepared by sublimation of the organic substances on clean metal surfaces in ultrahigh vacuum. Interestingly, we observed significantly lower hole injection barriers (0.2 - 0.4 eV) for DH6T on the metal surfaces than for 6T. We propose that the mechanism responsible for our observations is closely related to the "electron push-back effect" at metal/organic interfaces. Furthermore, the influence of molecular orientation will be discussed. Additionally, we demonstrate that the hole injection barrier at interfaces between 6T (DH6T) and metals can be further reduced by the formation of charge transfer complexes comprising tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

10:20am **EM+SS-WeM7 Top-contact Junctions for Molecules Electronics: Nano-transfer Printing**, *K. Ojima*, Osaka University, Japan; *K. Nakamatsu*, University of Hyogo, Japan; *Y. Otsuka, T. Matsumoto*, Osaka University, Japan; *S. Matsui*, University of Hyogo, Japan; *T. Kawai*, Osaka University, Japan

Recently, nanotransfer printing (nTP) attracts an attention as a method of producing the electrode. The electrode fabricated by nTP give the solutions for the problems of bottom contact-type electrode because electrodes are fabricated directly on the substrate after the deposition of molecules. In the previous reports, the nTP process needed chemical modification for the substrate in order to obtain well adhesiveness between the electrode and the substrate. This requirement has been serious limitation to fabricate molecular-scale devices. We have developed a nTP process for molecular devices without any modifications of substrate surfaces and evaluated the electrical properties of the electrodes fabricated by nTP. The use of the release agent enables us to print electrodes without any surface modification and heating the substrate. A test pattern of gold electrodes formed by the nTP on a DNA spread SiO₂/Si substrate was examine by AFM. We found that the resistivity of a line of gold electrode is nearly equal to that of bulk gold. We also examined the electric contact between the electrodes and molecules using Kelvin force microscopy (KFM) under applying bias voltage to the electrode/molecules junctions. We will present the images of electric potential distribution for the junctions.

10:40am **EM+SS-WeM8 Orbital Alignment and Chemical Interaction at Macro-Molecular Contacts**, *M.M. Beerbom, B. Lagel, J.P. Magulick, A.J. Cascio, R. Schlaf*, University of South Florida

Our experiments aim at the determination of the chemical and electronic structure of interfaces between macro-molecules and inorganic materials to determine charge injection barriers across the interfaces, the electronic structure of the highest occupied molecular orbitals (HOMO), and the chemical interaction between the materials in contact. Photoemission spectroscopy (PES) was used in combination with multi-step in-situ

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deposition of macro-molecular materials on inorganic substrates. PES characterization between deposition steps yields a sequence of spectra allowing the determination of the orbital line-up. Multi-step deposition was achieved using either a unique electrospray thin film deposition system, or a glove-box based deposition procedure. This allowed the fabrication of pure and non-contaminated interfaces suitable for PES measurements. Results from a series of experiments on poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV),¹ ribonucleic acid (RNA²) and L-cysteine (amino acid)³ interfaces will be presented. The electronic and chemical structure of these interfaces will be discussed as well as the measurement technique.¹ N. Dam, M.M. Beerbom, J.C. Braunagel and R. Schlaf: "Photoelectron Spectroscopic Investigation of In-Vacuum Prepared Luminescent Polymer Thin Films Directly From Solution", *J. Appl. Phys.* 97(pp.024909 (2005)).² N. Dam, B.V. Doran, J.C. Braunagel and R. Schlaf: "Charge injection barriers at a ribonucleic acid/inorganic material contact determined by photoemission spectroscopy", *J. Phys. Chem.* 109(2), pp.748-756 (2005).³ M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", *Langmuir Articles ASAP*, (2005).

11:00am **EM+SS-WeM9 Self-assembled Monolayers with Reactive Endgroups: Studies of Inorganic-Organic Interfaces and the Initiation of Top Contact Formation**, A. Dube, M. Sharma, A.S. Killampalli, J.R. Engstrom, Cornell University

Self-assembled monolayers (SAMs) have attracted considerable interest over the past several years in the field of molecular electronics. In such applications two interfaces become important, and understanding the formation of both is critical to effectively making use of SAMs in these devices. While formation of the bottom contact is a well studied area, the formation of top contacts is an immature field. We have been examining the reactions of transition metal coordination complexes, such as $Ti[(CH_3)_3Si]_2(CH_3)_2$ and $Ti[(CH_3)_3Si]_2(CH_3)_2$, with SAMs possessing different head group chemistries [e.g., $RSiCl_3$ on SiO_2 , R-(thiophene) on Au] and endgroup functionalities (e.g., $-CH_3$, $-NH_2$ and $-OH$) in order to develop an understanding of interface and contact formation. In this presentation we will highlight our most recent work that includes the self-assembly and reactions of functionalized molecular wires (thiophenes with conjugated ethynyl-phenylene backbones) adsorbed on Au using in situ angle resolved x-ray photoelectron spectroscopy (ARXPS). Here we find that the saturation density of the SAM increases from ~ 2.1 to 3.4×10^{14} molecules/cm² as the length of the conjugated backbone is roughly doubled. More importantly, these layers, which possess an isopropylamine endgroup, react via ligand exchange with $Ti[(CH_3)_3Si]_2(CH_3)_2$ even at -50 °C, forming a structure that has a Ti:SAM stoichiometry of $\sim 1:2$. ARXPS shows conclusively that these Ti coordination complexes bond with the SAMs exclusively at the isopropylamine group, and can seed additional deposition of the top contact. We will discuss the importance of these and other results concerning what they say about designing an effective means to make top contacts to molecular monolayer structures.

11:20am **EM+SS-WeM10 Observation of Interface Gap-State between Pentacene Molecules and Gold Metal by Scanning Tunneling Spectroscopy**, Y.J. Song, S.H. Kim, Y. Kuk, K. Lee, J. Yu, Seoul National University, Korea

Pentacene has been studied widely as a candidate for an organic thin film transistor (OTFT) because of its high mobility, and easy processing on various substrates. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the electronic structure of a single pentacene molecule adsorbed on Au(100) surface with one dimensional spatially-resolved scanning tunneling spectroscopy (1D SR-STs) to map position-dependent local density of states (LDOS).¹ In the geometry of metal-pentacene-metal transport measurement with a single crystal or a thin film pentacene, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. Au(100) surface was chosen since it offers both near-hexagonal and square symmetry, depending on a location of the (5x20) reconstruction. We measured SR-STs at various sites on the Au(100)-(5x20) surface. Unlike previously observed spectroscopy results on an insulator surface,² two dominant features are clearly resolved in the HOMO-LUMO gap of the spectroscopy: 1) Au surface state peaks of which

energy level is position independent, and 2) a HOMO derived gap state which depend on the registry of the pentacene molecule on the substrate. We expect that these gap states work as a scattering center and change the barrier height between metal contact and organics in the transport measurement. A density functional theory (DFT) calculation confirms our observation.¹ Jinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara and Young Kuk, *Nature (London)* 415, 1005 (2002).² Jascha Repp, Gerhard Meyer, Sladjana M. Stojkovic', Andre' Gourdon and Christian Joachim, *Phys. Rev. Lett.* 94, 026803 (2005)

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Room 202 - Session SS+EM-WeM

Self-Assembled Monolayers

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

8:20am **SS+EM-WeM1 Investigation of Mixed Fluorocarbon/Hydrocarbon Self-Assembled Monolayers on Au by Reactive Ion Scattering Spectrometry**, X. Yang, University of Arizona; S. Ravindran, University of Texas; A. Graham, K. Nebesny, University of Arizona; T.R. Lee, University of Houston; N.R. Armstrong, V.H. Wysocki, University of Arizona

A series of mixed self-assembled monolayers (SAMs) of CF_3 and CH_3 were prepared on polycrystalline gold. Surface composition and crystallinity were first examined by XPS, FT-RAIRS and contact angle. Homogeneously mixed and well-ordered surfaces were formed. Results showed that surface composition followed solution composition uniformly. Reactive Ion Scattering Spectrometry (RISS) utilizing low-energy (<100eV) ion-surface collisions was used to investigate the mixture monolayers. Experiments are carried out in a tandem quadrupole mass spectrometer. Precursor ions selected by the first quadrupole collide onto the surfaces at given collision energies. Neutralization and fragmentation of projectiles, ion-surface reaction and sputtering of surface species occur upon collision of the projectile ions with the surface. Product ions are extracted and analyzed by the second quadrupole. Benzene, tungsten hexacarbonyl and d4-pyrazine positive radical ions were used as projectile ions. As $C_{16}F_2$ concentration increases on the surface, projectile neutralization decreases, the amount of methyl/hydrogen abstraction decreases non-linearly, and linear increases of translational to internal energy conversion upon collision of either benzene or tungsten hexacarbonyl are shown. RISS shows high sensitivity to composition and homogeneity of surfaces.

8:40am **SS+EM-WeM2 Surface Bonding and Dynamical Behavior of CH_3 on Au(111)**, P. Maksymovych, University of Pittsburgh; D.C. Sorescu, U.S. Department of Energy; D.B. Dougherty, J.T. Yates, Jr., University of Pittsburgh

Alkanethiols are often used for the growth of self-assembled monolayers, which are ordered 2-D molecular films covalently bonded to a substrate, typically a gold surface. The bonding of alkanethiols to gold has remained a controversial issue. In particular, the bonding of the undissociated alkanethiols has not been addressed at the atomic scale so far. We have studied adsorption and surface chemistry of the smallest alkanethiol, CH_3 on the Au(111) surface using the Scanning Tunneling Microscopy (STM) at 5K and Density Functional Theory (DFT). It has been established that CH_3 adsorbs and desorbs without dissociation. Using the STM, it was found that CH_3 adsorbs on top of an Au atom on the defect-free surface, and undergoes hindered rotation at 5K. The barrier to rotation obtained by DFT calculations is ~ 0.1 kcal/mol. The STM image of the rotating molecule has a shape of a flower with six petals. The pattern suggests that the potential minima directions occur for the rotating molecule at the six hollow sites surrounding the atop adsorption site. Furthermore, selective site occupation was observed on the length-scale of the herringbone reconstruction of the Au(111) surface. At very low coverage, the CH_3 molecule was found to preferentially adsorb on the intrinsic defective sites on the surface, such as the herringbone "elbows" and random atomic step sites. At higher coverage preferential adsorption occurred on the fcc-stacked regions of the herringbone reconstruction. The latter is explained by the variation of the surface stress across the Au(111) surface due to the herringbone reconstruction, which causes the mobile CH_3 molecules to select the most exothermic adsorption sites available at various coverages. We thank the W. M. Keck Foundation and NEDO (Japan) for financial support of this work.

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9:00am **SS+EM-WeM3 Diffusion and Aggregation of Thiol-Linked Organic Molecules on a Cu(111) Surface**, *K.L. Wong, K.-Y. Kwon, X. Lin, L. Bartels*, University of California at Riverside

We have investigated the adsorption geometry and the detailed surface dynamic behavior of benzenethiol (BT) molecules on a Cu(111) surface at low temperatures (50-60K). We chose BT as a model system, because it contains both the aromatic moiety and the thiol linker common in molecular molecules, yet it is sufficiently small to be treated at high resolution experimentally and theoretically. The BT molecule adsorbs onto Cu(111) in two types of adsorption sites. In both cases the sulphur atom is believed to be adsorbed near the fcc hollow site while the benzene group is located near parallel to the surface. The more stable adsorption configuration (I) have the benzene ring centered near an hcp hollow site while the less stable adsorption configuration (II) have the benzene ring centered near an on-top site. The molecule can change adsorption configurations by rotation around the sulphur atom. Rotation from (II) to (I) occurs more rapidly than in the opposite direction. In addition to rotations the molecule can diffuse to nearby adsorption site. The sulphur atom jumps to one of six nearby adsorption sites along the high symmetry axis of Cu(111) while the orientation of the molecule with respect to the substrate remains the same. The rate of rotations and translations has been measured at different temperatures in the range 50-60K. An Arrhenius fit to the measured data yields rotations and diffusion barriers of 120meV, 130meV and 150meV respectively. DFT calculations show good agreement with the STM data. At higher coverages the adsorbed BT molecules form stable aggregates. No stable aggregates larger than 7 molecules were found, instead the density of evenly distributed 7-molecule aggregates increases with the coverage. Abundance histograms of aggregates with different sizes and configurations reveal a delicate balance between molecule-substrate and molecule-molecule interactions.

9:20am **SS+EM-WeM4 Tunneling Spectroscopy of Self-Assembled Monolayers of 1-adamantanethiolate on Single Crystal Metallic Substrates**, *A.R. Kurland, A.A. Dameron, P. Han, S.U. Nanayakkara, P.S. Weiss*, The Pennsylvania State University

We measure local barrier height and differential conductance using ultrahigh vacuum scanning tunneling microscopy (STM) at 4 K to investigate the work function and local density of states, respectively, of individual adamantanethiolate molecules on a range of single crystal metallic substrates. These techniques allow us to probe specific electronic characteristics while simultaneously resolving the molecular lattice of the adamantanethiolate monolayers. Previously, we have shown that adamantanethiolate molecules form well-ordered hexagonally close-packed monolayers on the Au{111} surface. The complex and highly symmetric cage structure of adamantanethiolate results in weaker intermolecular interactions than those of alkanethiolate self-assembled monolayers. Taking advantage of these properties, we have implemented adamantanethiolate molecules in thin-film molecular lattices and as nanolithography patterning inks. We aim to exploit and to incorporate the unique physical and electronic interactions of adsorbed adamantanethiolate to understand and to tailor self-assembled nanostructures.

9:40am **SS+EM-WeM5 Interaction Pathways of Vapor Deposited Metal Atoms with Self-Assembled Monolayers**, *D. Allara, N. Winograd*, Pennsylvania State University; *A.V. Walker*, Washington University; *T. Tighe, T. Daniel, O. Cabarcos, S. Uppili*, Pennsylvania State University

INVITED

With rapid progress being made in the fabrication and testing of molecule-based electronic devices in the past several years one of the critical issues that has arisen is the character of the metal-molecule interfaces and interphases of vapor-deposited top contact device structures. Results will be discussed that show a broad strategy for developing correlations between the interactions of a wide variety of metals with a range of alkanethiolate/Au{111} self-assembled monolayers (SAMs) carrying varied terminal groups. The metals include inert coinage metals, one-electron donor alkali metal and aggressively reactive metals such as Ti. The SAMs range from those with hydrocarbon surface character to others with high electron acceptor character (-NO₂, C=N, C=O moieties) and including "solvating" types of groups such as -OCH₃. The use of 4-5 different in-situ surface characterization tools augmented by DFT calculations aids greatly in achieving incisive information ranging from metal atom surface scattering to the evolution of the metal-molecule interface chemistry and the metal film morphology. Details include the distribution of metal and reaction products throughout the SAM structure, both laterally and extending to the substrate interface. Coupling this

information with the character of the SAM/base electrode interface can provide critical information to aid fundamental interpretations of device behavior.

10:20am **SS+EM-WeM7 Replicative Generation of Electrode Structures by SAM-templated Electrometallization**, *I. Thom, G. Haehner, M. Buck*, University of StAndrews, UK

Self-assembled monolayers (SAMs) of thiols provide a convenient way to modify electrode surfaces and, thus, to control charge transfer at an electrochemical interface. Adjustment of electrode properties from conducting to blocking is achieved by variation of the SAM forming molecules. Since a variety of methods is available to pattern thiol monolayers, this type of SAM can serve as templates to confine electrochemical processes, e.g. metal deposition. However, in addition to the control of charge transfer, SAMs serve also to control adhesion between deposit and electrode and, therefore, make the generation of metal structures by electrochemical deposition and subsequent transfer to a different substrate possible. Copper structures were produced by electrochemical deposition onto SAM-modified polycrystalline gold electrodes. Selective metal deposition was achieved by use of thiols which differ in their electrochemical blocking properties, namely hexadecane thiol and @omega@-(4'-methyl-biphenyl-4-yl)-methanethiol. After deposition the metal patterns were easily transferred to an insulating substrate by glueing. Characterization of the transferred structures with atomic force microscopy shows that the flatness of the metal surface is essentially determined by the initial SAM carrying substrate electrode. Since the thiol pattern on the substrate electrode remains intact, it can be repetitively used. Therefore, the process allows an easy and fast fabrication of high quality electrode patterns.

10:40am **SS+EM-WeM8 Alkylidyne Self-Assembled Monolayers on Pt(111): A Novel System for Molecular Electronics Applications**, *M. Yang, A.R. Laracuente, L.J. Whitman*, Naval Research Laboratory

Although many alkanethiols form well-understood self-assembled monolayers (SAMs) on gold, such systems are of limited utility for molecular electronics applications given the incompatibility of gold with conventional silicon devices. Moreover, it is now widely recognized that the gold-sulfur bond inhibits electrical transport between the substrate and the bound organic molecules. Because of these issues, there has been recent interest in more compatible metals such as Pd and Pt, along with non-thiol bonding schemes for organic molecules. We are developing a new type of SAM/metal system based on direct carbon-to-metal bonding. When 1-hexene (C@sub6@H@sub14@) is vapor-deposited on clean Pt(111) in ultra-high vacuum, it converts into hexylidyne (C@sub6@H@sub11@) to form a self-assembled monolayer (SAM) with an upright geometry. Scanning tunneling microscopy studies show that the hexylidyne SAM on Pt(111) is a commensurate (3x3) overlayer. We have also investigated the influences of pressure, temperature, and coadsorbed hydrogen on the formation of the alkylidyne SAMs. Given that many of the organic molecules of potential use for current transport are alkanes and perylenes, direct carbon-metal bonding may provide the most desirable metal-molecule junction. Therefore, we believe this system has significant potential for developing molecular electronic devices.

11:00am **SS+EM-WeM9 Vertically Aligned Chromophoric Molecular Assemblies on a Si Surface**, *G.G. Jernigan, M.F. Pepitone, J.S. Melinger, O.-K. Kim*, US Naval Research Laboratory

Strong motivation for the development of molecular devices is the ability to synthetically create a molecule with desired optical and electronic properties through the linkage of different chemical moieties. The challenge remains, however, to integrate such a molecule with a physical device. Molecules can take various physical conformations and can interact with nearby molecules or surfaces resulting in a loss of optical and electronic properties. We have developed a method for encapsulating a 4-[4-(Dimethylamino) styryl]-1-docosylpyridinium bromide (DASP) chromophore in a helical amylose sheath to produce a supramolecular assembly as a molecular device. The benefits of the supramolecular assembly formation are attributed to the ability of the amylose to rigidify the conformation of the DASP molecule, to individually isolate DASP molecules, and to prevent the DASP molecules from interacting with other DASP molecules to form aggregates. When DASP forms aggregates, the fluorescence is quenched, but when DASP is encapsulated by amylose, the fluorescence intensity is maximized. We report that when the supramolecular assemblies are self-assembled onto a Si surface that DASP emits a strong fluorescence with a spectrum that is similar to that found in solution. More importantly, AFM images show that the assemblies

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vertically self align at near monolayer coverage on the Si surface. We have subsequently linked a viologen species (electron acceptor) to the DASP (electron donor) through various hydrocarbon chain spacers resulting in distant-dependent electron transfer. We report this system as the basis for a molecular photodiode.

11:20am **SS+EM-WeM10 Laser Activation-Modification of Surfaces**, G. Jiang, M.C. Asplund, M.R. Linford, Brigham Young University

We have recently developed a new and extremely rapid method for simultaneously functionalizing and patterning surfaces, which we term Laser Activation-Modification of Surfaces, or LAMS. This method consists of wetting a surface, e.g., Si or Ge, with a chemical and firing an intense, nanosecond pulse of laser light (355 or 532 nm) through the liquid onto the surface. The energy ablates a thin layer from the surface, exposing a highly reactive surface that appears to react instantaneously with the liquid it is in contact with. LAMS on silicon has been demonstrated with homologous series of 1-alkenes and 1-haloalkanes, and an epoxide and an alcohol. Unreactive compounds, such as octane and perfluorodecalin, also react in this manner; LAMS on Si with octane results in a functionalized surface. Surface modification is confirmed by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and chemical reactivity. Functionalized feature dimensions and morphology are shown by atomic force microscopy and imaging ToF-SIMS.

11:40am **SS+EM-WeM11 Temperature-Dependent Branching of Photochemical Reactions in Organic Layers and Biological Systems**, M. Zharnikov, A. Shaporenko, Universität Heidelberg, Germany; A. Baumer, Walter Schottky Institut, Germany; D. Menzel, Technische Universität München, Germany; P. Feulner, Technische Universität München, Germany
Radiation-induced damage represents a severe constraint for the characterization of organic materials, biological macromolecules, and cells by advanced electron or x-ray spectroscopy and microscopy. A possibility to reduce irradiation-induced degradation is cooling of the samples down to cryogenic temperatures. However, although the protecting effect of sample cooling against radiation damage is empirically well demonstrated, no detailed knowledge on its exact microscopic mechanism exists as yet. It is commonly assumed that the main effect is simply hindrance of mass transport in the object, whereas the basic irradiation-induced bond cleavage is believed to be unaffected. To prove this hypothesis we studied radiation damage of self-assembled monolayers, which are prototypes of thin organic layers and highly organized biological systems. We demonstrate that the effect of cooling is twofold. It freezes the structure, but by decreasing the mobility of fragments it also changes the branching of various photochemical reactions, thereby strongly modifying the cross sections as well as the products of irradiation induced processes. Two limiting cases could be identified. Reactions involving transport of single atoms and small fragments proceed nearly independent of temperature. Reactions requiring transport of heavy fragments are, however, efficiently quenched by cooling. We speculate that bonds can recombine if the fragments are forced to stay in place due to their reduced mobility at low temperatures. The results have direct implications for cryogenic approaches in advanced electron and x-ray microscopy and spectroscopy of biological macromolecules and cells.

Surface Science

Room 200 - Session SS1-WeM

Growth and Alloying of Surfaces

Moderator: K.F. McCarty, Sandia National Laboratories

8:20am **SS1-WeM1 Surface Alloy Compositions with Temporal and Spatial Resolution**, J.B. Hannon, IBM Research Division; J. Sun, University of New Hampshire; G.L. Kellogg, Sandia National Laboratories; K. Pohl, University of New Hampshire

Controlling the composition of thin-film alloys is critical in a wide range of technologies. However, measuring alloy compositions at surfaces is difficult. Quantitative information on surface alloy compositions can be obtained from analysis of low-energy electron diffraction intensity versus energy spectra (LEED-IV). However, so far the structure and composition had to be assumed as spatially uniform. In this presentation we will describe low-electron energy microscopy (LEEM) studies on the formation of the well-known CuPd surface alloy phase grown on Cu(001). We will show how the presence of steps in the growth process makes the alloy layer inherently inhomogeneous. These variations in the CuPd alloy composition introduce strong measurable changes in the electron

reflectivity in the regions around steps. By analyzing spatially resolved IV curves taken every 10 nm along a scan line normal to a step, we have determined the local surface alloy composition in the first 3 layers by using the average t-matrix approximation on a $c(2 \times 2)$ grid. In the process we are simultaneously optimizing both structural and non-structural parameters, while special emphasis is given to characterize the individual error bars of the method. We have investigated the composition on the terrace, far from steps, and the step-induced inhomogeneous structure caused by the step-flow growth. Depositing Pd at 500 K will cause an exponential increase of the Pd concentration with time and the formation of a $c(2 \times 2)$ Pd checkerboard structure in the 2nd Cu layer up to a 50% Pd concentration; far from the steps where the alloy is spatially uniform. However, during growth the steps flow over the 2nd layer Pd alloy, bury it and convert it to a 3rd layer alloy. This 3rd layer Pd is immobile and its concentration increases exponentially toward the step edge along the upper terrace, in agreement with the step-flow-growth model.

8:40am **SS1-WeM2 Formation and Vibrational Entropy-Driven Disordering of Mo(100) and W(100) Surface Alloys**, K.L. Man, Y.J. Feng, C.T. Chan, Hong Kong University of Science and Technology; M.S. Altman, Hong Kong University of Science and Technology, Hong Kong

Atoms that are deposited on a surface of a dissimilar material may either remain on the surface or they may become incorporated in a surface or bulk alloy. Although the $T = 0$ energetic differences between alloy and overlayer structures can now be understood from first principles in many systems, entropy differences should also be revealed in the formation and stability of alloy versus overlayer structures. However, the entropic contribution to the system free energy is much less well understood than the energetic. The formation and stability of Cu, Ag and Au-induced $c(2 \times 2)$ alloys at the Mo(100) and W(100) surfaces have been investigated with low energy electron microscopy and diffraction. The dependence of the $c(2 \times 2)$ diffraction intensity upon metal deposition flux reveals that alloy formation is governed by atomistic processes that are analogous to those that dictate overlayer island nucleation. A second-order order-disorder transition is also observed that converts the surface from ordered alloy to disordered overlayer structure. Combined with knowledge of energetics obtained from first principles calculations, a comparison of disordering temperatures for alloys of the different metal species and substrates provides information on the vibrational entropic contribution to the system free energy. Effective Debye temperatures for metal adatoms are determined that are substantially lower than bulk values, but exhibit the expected mass dependence. Knowledge of the vibrational properties of metal adatoms should also be relevant to other common surface phenomena such as diffusion and desorption.

9:00am **SS1-WeM3 Bulk/Surface Mass Exchange and the Special Role of Bulk Dislocations in the Growth of NiAl Alloy**, J.P. Pierce, K.F. McCarty, N.C. Bartelt, Sandia National Laboratories

When aluminum atoms are deposited on the surface of an Al-depleted NiAl crystal at high temperatures (> 900 K), new layers of NiAl alloy grow on the surface. We directly observe the appearance of new alloy by watching atomic steps advance across the surface using low-energy electron microscopy (LEEM). This behavior means that while Al atoms are delivered to the surface by our evaporator, Ni atoms are supplied to the surface by the bulk of the crystal. The competition in the arrival rates of these species determines how the surface evolves. At low temperatures (< 750 K), Ni atoms are unable to diffuse to the surface fast enough to accommodate the incoming Al atoms, so the Al atoms form a film on top of the alloy. At intermediate temperatures (750 to 900 K), we find that dislocations play a special role in transporting mass between the surface and the bulk. Al deposition causes the composition (i.e., the relative concentration of Al and Ni) at the surface to reach a critical level at which the points where bulk dislocations terminate on the (110) surface begin to move linearly. The dislocations provide a channel for mass exchange between the surface and the bulk; as the dislocations move, new crystal is left in their wake. As predicted by the one-dimensional diffusion equation, we find that the duration of Al exposure required bring the surface to the critical composition for dislocation motion grows as the inverse square of the Al flux. This confirms that the behavior on the surface is indeed limited by the diffusion of atoms through the bulk. We use our observations to identify the point defects that allow the Ni and Al atoms to diffuse and use the one-dimensional diffusion model to determine how the depth profile of the relative concentration of Ni and Al atoms evolves with time as the crystal tries to equilibrate. 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.

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9:20am **SS1-WeM4 Real-Time Microscopy of Phase Transitions on Pb/Ge(111)**, *S. Chiang, Y. Sato*, University of California, Davis

Using low energy electron microscopy (LEEM), we have elucidated the phase diagram for the growth of Pb on Ge(111). The Pb layer can form two stable $\sqrt{3}\times\sqrt{3}$ phases on the surface, less dense $\sqrt{3}\times\sqrt{3}$ and denser 2×2 phases. As Pb is deposited on Ge, the Pb atoms substitute into the top layer, causing released Ge atoms to form into $c(2\times 8)$ adatom islands, with the size and density of these Ge islands controllable by the substrate temperature. With 11.6 eV electrons at 300C, we see the growth of the white (1×1) phase with respect to the darker $\sqrt{3}\times\sqrt{3}$ phase in a coexistence region. During the reversible $\sqrt{3}\times\sqrt{3}$ to (1×1) phase transition, we discovered a novel phase separation mechanism. Above the 1.33ML $\sqrt{3}\times\sqrt{3}$ saturation coverage, a sharp first order phase transition is observed near 295C. For Pb coverage just <1.33 ML, the $\sqrt{3}\times\sqrt{3}$ to (1×1) phase transition is no longer sharp, with the $\sqrt{3}\times\sqrt{3}$ and (1×1) phases coexisting and the transformation occurring from 232C to 181C. Reducing coverage by ~ 0.01 ML causes a dramatic change. When the transition starts, small domains of the new phase appear and disappear, due to fluctuations between the two phases. As the initial domains stabilize in the new phase, additional domains appear and fluctuate until the whole surface is completely transformed. By using statistical mechanics analysis, we attribute the fluctuating domains to thermal fluctuations of the density of Pb atoms within a domain. By comparing LEEM images of the $\sqrt{3}\times\sqrt{3}$ and (1×1) phases during the phase transition between $(\sqrt{3}\times\sqrt{3} + (1\times 1))$ and $(\sqrt{3}\times\sqrt{3} + 2\times 2)$, the Pb coverage of the (1×1) phase at the eutectic point was determined to be ~ 1.29 ML. N. Bartelt, Sandia National Laboratories, Livermore, CA.

9:40am **SS1-WeM5 Self-Organized Growth and Magnetism of Nanostructures at Surfaces**, *H. Brune*, École Polytechnique Fédérale de Lausanne - EPFL, Switzerland **INVITED**

We will discuss the state-of-the-art of self-organized atomic beam growth at single crystal surfaces enabling one to create well ordered superlattices of metal islands with sizes going all the way down to the single atom limit. We will focus on mutual interactions between adsorbed atoms mediated by Friedel oscillations in the 2D electron gas of a surface state, and on static templates with a periodic modulation of the binding energy for the adsorbed species. The templates to be discussed are strain relief patterns in thin films of metals, semiconductors, oxides, and nitrides. We then show model systems suited to explore the ultimate density limit of magnetic information storage. These are Co islands self-assembled on Au(788). The temperature dependence of the zero-field susceptibility χ shows that the homogeneity in the anisotropy K and in the moment M would permit single particle bits, and that mutual interactions between the monodomain particles are absent up to densities of at least 26 Tera particles/in². We further show results on the anisotropy of bimetallic islands as a function of their composition.

10:20am **SS1-WeM7 Steering Induced Nanopatterning: Super Poisson Growth at Grazing Incidence**, *H. Wormeester, F.L.W. Rabbering, B. Poelsema*, University of Twente, The Netherlands

Analysis of high-resolution LEED data of 40 ML Cu on Cu(001) deposited at various polar angles led to the conclusion that attractive forces between the surface and the incoming particles have a dramatic steering effect on the trajectory of the particle. Incoming particles are attracted towards protruding structures leading to increased roughness and the formation of 1D nanopatterns at grazing incidence deposition. Already in the submonolayer coverage range consequences of the steering effect is observed for grazing incidence deposition. The steering induced heterogeneous distribution of the incoming flux has been modeled by a combination of long range Van der Waals forces and EAM calculations. The resulting trajectories have been combined with kMC simulations taking into account a large variety of intra and inter layer diffusion processes. The simulations are in good accordance with diffraction measurements up to 40 ML at both normal and grazing incidence. The evolution of the 1D nanopattern at glancing incidence deposition in terms of the distance between the ripples, the anisotropy and the roughness has been studied. The roughness evolves from a layer-by-layer fashion in the initial phase towards a strongly roughened interface above 10 ML. At 30 ML the roughness turns out to be even larger than for a Poisson distribution, i.e. super Poisson growth is observed. The steering effect thus implies the necessity of a very different view for understanding the morphology development in growth at oblique incidence.

10:40am **SS1-WeM8 Ostwald Ripening of Manganese Silicide Islands on Si(001)**, *M.R. Krause, A. Stollenwerk, J. Reed, V.P. LaBella*, University at Albany SUNY

Theoretical considerations suggest that epitaxial MnSi thin films should order ferromagnetically on Si(001) and it has been demonstrated that Si can be made ferromagnetic well above room temperature by Mn ion implantation. These recent discoveries indicate that the Mn-Si system may have potential to be utilized as a spin injector in future spintronics devices. Therefore the deposition of Mn onto Si(001) in the submonolayer regime has been studied with scanning tunneling microscopy (STM) to gain insight into the bonding and energetics of Mn with Si. The as deposited Mn films at room temperature are unstructured. Upon annealing to 300-500°C no smooth films but clusters of Mn or Mn_xSi_y form while between the clusters the Si(001)-(2x1) reconstruction becomes visible. With increasing annealing time the density of clusters per surface area decreases while the average size of the remaining clusters increases. The time dependence of the coarsening shows the typical characteristics of Ostwald Ripening (OR). The cluster density and average cluster size will be presented as a function of annealing time for different initial Mn coverages. The results will be discussed within the framework of the OR theory. H. Wu, et al. Phys. Rev. Lett. 92 237202 (2004). M. Bolduc et al. Phys. Rev. B 71 033302 (2005).

11:00am **SS1-WeM9 Self-assembly of Aperiodic Nanostructures using Quasicrystal Surfaces as Templates**, *R. McGrath*, The University of Liverpool, UK **INVITED**

Quasicrystals are metallic alloys which possess long-range order but not periodicity; hence they may display structural symmetries not observed in periodic materials. The surfaces of these materials offer opportunities for the fabrication of nanostructures and thin films which themselves have unusual symmetries and structures. In turn, measurements of such nanostructured systems may offer insights into the larger question of the relationship between physical properties and aperiodicity. Several such systems, ranging from individual atoms to nanoclusters to thin films, have been fabricated and are under investigation in our laboratory. The growth of Si on quasicrystal surfaces is one recent example. On the AlPdMn quasicrystal, at submonolayer coverages, individual Si atoms occupy a unique adsorption site; thus the Si atoms can be considered to be arranged in a two-dimensional quasiperiodic array. On decagonal AlNiCo, the Si atoms form 5-fold nanoclusters, again indicative of a preferred adsorption site. Another spectacular example is that of an ultrathin film grown by the deposition of copper atoms on the five-fold surface of the icosahedral Al₇₀Pd₂₁Mn₉ quasicrystal. STM images show that the in-plane structure comprises rows having separations of $S=4.5\text{Å}\pm 0.2\text{Å}$ and $L=7.3\text{Å}\pm 0.3\text{Å}$, whose ratio is the golden mean $\tau=1.618\dots$ within experimental error. The sequences of such row separations form segments of terms of the Fibonacci sequence, indicative of the formation of a pseudomorphic Cu film. Finally, we have recently demonstrated that pseudomorphic films can also be grown using magnetic elements such as Co, Fe and Ni. Atoms in a quasiperiodic pattern are predicted to form new types of frustrated structures; such films therefore offer the possibility of observing these novel magnetic effects. J. Ledieu, J.T. Hoeft, D.E. Reid, J.A. Smerdon, R.D. Diehl, T.A. Lograsso, A.R. Ross and R. McGrath, Phys. Rev. Lett. 92 (2004) 135507.

11:40am **SS1-WeM11 Coexistence of Periodic and Quasiperiodic Order in a Two-Fold Al-Ni-Co Decagonal Quasicrystal Surface**, *J.Y. Park, D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory; *R.A. Ribeiro, P.C. Canfield, C.J. Jenks, P.A. Thiel*, Iowa State University

The atomic structure of the two-fold surface of a decagonal Al-Ni-Co quasicrystal has been investigated using scanning tunneling microscopy (STM). In the bulk the decagonal quasicrystal is composed of quasiperiodic planes that are periodically arranged. Atomically resolved scanning tunneling microscopy images of the 2-fold (10000) plane reveal the presence of atomic rows along the 10-fold direction with an internal periodicity of 0.4 nm. The spacing between the parallel rows is aperiodic, with distances following a Fibonacci sequence and exhibiting inflation symmetry. The bias polarity dependence of the STM images reveals three electronically-different types of atomic rows. A bulk model for Al-Ni-Co shows excellent agreement with these STM observations, and indicates that Al sites have a higher tunneling probability than transition metal sites. These data are compared with previous results for both the 10-fold and 2-fold surfaces.

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Surface Science

Room 203 - Session SS2-WeM

Reactions on Metals & Oxides

Moderator: B.E. Koel, University of Southern California

8:20am **SS2-WeM1 Reactivity of Oxygen on Au(111) in CO Oxidation, B.K. Min, A.R. Alemozafar, D.S. Pinnaduwaige, X. Deng, C.M. Friend**, Harvard University

Characteristics of oxygen on Au(111) related to reactivity in carbon monoxide oxidation were investigated by X-ray photoelectron spectroscopy (XPS), high resolution electron loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). Oxygen was deposited on the Au(111) surface between 200 K - 400 K via exposure to ozone. Depending on the adsorption temperature, different characteristics of oxygen (chemisorbed and oxidic) and surface morphologies were observed. The reactivity of the oxygen-covered Au(111) surface is strongly dependent on reaction temperature; highest reactivity is observed at 200 K. Additionally, oxygen deposited at 200 K is more reactive than oxygen deposited at 300 K and 400 K. These results suggest that both reaction temperature and characteristics of oxygen are important for the reactivity of Au(111) in carbon monoxide oxidation.

8:40am **SS2-WeM2 Modeling of Nanoscale Spatiotemporal Behavior in CO-oxidation on Pd(100), D.-J. Liu, J.W. Evans**, Iowa State University

For CO-oxidation on metal surfaces, a few STM studies have begun to explore nanoscale spatial organization in titration reactions, and FIM studies have revealed propagation of near-atomically sharp reaction fronts. However, there has been almost no realistic atomistic modeling of such processes. Thus, we have developed such a model for CO-oxidation on Pd(100) exploiting DFT calculations and experimental data, e.g., on adspecies ordering, to accurately determine the small but significant lateral interactions between adspecies. Efficient kinetic Monte Carlo algorithms are developed to study model behavior. Below 300 K, the system can be characterized by coadsorption of CO and oxygen with different ordering structures. Between 300 K and 350 K, reaction occurs involving sharp moving fronts between domains of CO and oxygen. In this regime, chemical diffusion of CO is greatly inhibited due to strong interactions between adsorbates. (At higher temperatures, the interface between CO- and oxygen-rich domains becomes an extended chemical wave, familiar from PEEM studies, the profile reflecting the coverage dependent CO diffusion.) Finally, for nanoscale systems (such as field emitter tips or supported metal clusters), fluctuation-induced transitions between reactive and near-poisoned steady states were also analyzed.

9:00am **SS2-WeM3 Surface Reactivity Tailored by Electron Confinement or Surface Modifiers Probed at Micro and Nano-Scales, M. Kiskinova**, Sincrotrone Trieste, Italy

INVITED

Most of the attempts to tailor the surface reactivity have focused on the creation of specific surface structures, where electronic perturbations are induced, or by chemical modification of the surface properties by adding small amounts of substances. Recently it has been shown that the chemical specific imaging, combined with laterally resolved structural characterizations is of vital importance for understanding key factors controlling the processes at the surface of complex systems and the related to that local reactivity. In the talk selected results obtained using chemical specific imaging, photoelectron micro-spectroscopy, low energy electron microscopy and scanning tunnelling microscopy will be presented and discussed. The effect of electron confinement in ultrathin films will be illustrated for Mg films with varying thickness at micrometer scales; they show sensible difference in the local oxidation rate, correlated to the periodic changes in the density of electronic states induced by quantum-well states crossing the Fermi level of the Mg film. @footnote 1@ The complexity of the realistic systems, where a rich variety of self-organized micro and/or nano-structures may form and coexist under reaction reactions will be illustrated using the results obtained with Rh surfaces modified with potassium or other metals. @footnote 2,3@. It will be shown that stabilization of the substrate surface reconstructions and mass transport driven self-reorganization processes are common phenomena, which may affect the composition and reactive properties of the surface at local microscopic scales. @FootnoteText@@@footnote 1@ L. Aballe et al, Phys. Rev. Lett. 93, 2004, 196103. @footnote 2@ S. G@um u@nther et al, J.Chem. Phys. 117, 2002, 2923119; ibid. 119, 2003, 12503; J. Phys. Chem. 2005, in press. @footnote 3@ A. Locatelli et al, J. Am. Chem. Soc. 127, 2005, 2351.

9:40am **SS2-WeM5 Rh-promoted Decomposition of Methanol Adsorbed on Cerium Oxide Thin Films, J. Zhou, D.R. Mullins**, Oak Ridge National Laboratory

Metal nanoparticles supported on single crystal oxides are important model systems for industrial catalysts. Research has found that the oxide substrates can greatly influence the catalytic activity of metal particles supported on them. In our study we have found that the reverse may also be true, i.e. that Rh nanoparticles may influence the thermal decomposition of methanol adsorbed on the oxide. All of the experiments were performed under UHV conditions by temperature programmed desorption (TPD) and synchrotron soft X-ray photoelectron spectroscopy (SXPS). Methanol decomposition was first carried out on the substrate ceria films to differentiate its chemistry from that when Rh is present. SXPS indicates that methanol deprotonates to form methoxy as the only intermediate on the ceria surface. On fully oxidized ceria, chemisorbed methoxy produced methanol and formaldehyde at about 560 K. However, on reduced ceria films methoxy decomposed further to produce primarily CO and H@sub 2@. When Rh nanoparticles were added to the ceria films, methoxy decomposed to CO and H@sub 2@ regardless of the ceria oxidation state and formaldehyde formation was suppressed. The desorption temperatures and intensities of CO and H@sub 2@ were found to be dependent on the reduction of the ceria films. These results indicate that the Rh promotes the decomposition of methanol adsorbed on the ceria and that decomposition may be influenced by the diffusion of methoxy intermediates across the oxide to the metal particles. Research sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

10:00am **SS2-WeM6 Adsorption of NO2 on Ultrathin @theta@-Al2O3/AlNi(100) Film: the Formation of Nitrite and Nitrate Species, J. Szanyi, E. Ozensoy, C.H.F. Peden**, Pacific Northwest National Laboratory

The interaction of NO2 with an ordered @theta@-Al2O3/NiAl(100) model catalyst surface was investigated using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The origin of the NOx uptake of the catalytic support (i.e. Al2O3) in a NOx storage catalyst is identified. Adsorbed NO2 is converted to strongly bound nitrites and nitrates that are stable on the model catalyst surface at temperatures as high as 300 and 650 K, respectively. The results show that alumina is not completely inert and may stabilize some form of NOx under certain catalytic conditions. The stability of the NOx formed by exposing the @theta@-Al2O3 model catalyst to NO2 adsorption increases in the order: NO2 (physisorbed or N2O4) < NO2 (chemisorbed) < NO2- < NO3-.

10:20am **SS2-WeM7 Correlation Between Electronic Structure and Chemical/Catalytic Reactivity of TiO@sub 2@(110) Supported Vanadia Catalysts, S. Lee**, Texas A&M University; G.W. Zajac, Innovene Corporation; D.W. Goodman, Texas A&M University

The adsorption and reaction of ethanol on model catalysts comprised of vanadium and vanadia deposited on rutile TiO@sub 2@(110) have been studied using temperature programmed desorption (TPD), X-ray and UV photoelectron spectroscopy (XPS and UPS), metastable impact electron spectroscopy (MIES), and low energy electron diffraction (LEED). Vanadium and vanadia films were prepared on TiO@sub 2@(110) under UHV conditions and the changes in their electronic properties were monitored following the adsorption and reaction of ethanol. Comparisons are made to Density of States generated from DFT calculations of small slabs of VO@sub x@/TiO@sub 2@ (Rutile) via the commercial codes of CASTEP and DMOL@super 3@ from Accelrys Inc. Dissociative adsorption of ethanol leads to the formation of ethylene at 650 K on TiO@sub 2@ supported vanadium. The activity for this reaction was found to depend markedly on the vanadium oxidation state.

10:40am **SS2-WeM8 Catalytic Activity of WO@sub 3@ Clusters on TiO@sub 2@(110): Trimerization of Formaldehyde, J. Kim**, Pacific Northwest National Laboratory; O.A. Bondarchuk, University of Texas, Austin; Z. Dohnálek, Pacific Northwest National Laboratory; J.M. White, University of Texas at Austin; B.D. Kay, Pacific Northwest National Laboratory

The catalytic activity of supported, high surface area transition metal oxides (TMO) catalysts have been extensively studied. In contrast, only a few studies have been conducted on transition metal oxide clusters supported on well-ordered, single-crystalline oxide surfaces. In this study, the catalytic activity of WO@sub 3@ clusters deposited on a well-characterized TiO@sub 2@(110) surface was examined. The clusters were deposited via direct, thermal evaporation of WO@sub 3@. This deposition

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technique provides a reliable, carbon free source of W in the (6+) oxidation state as shown by X-ray photoelectron spectroscopy (XPS). Related scanning tunneling microscopy (STM) studies reveal that 600 K-annealed WO₃ clusters are monodispersed and ~1 nm in diameter. Temperature programmed desorption (TPD) of N₂ reveals that the structure of WO₃ does not change significantly between 400 - 600 K. We have examined the adsorption of formaldehyde (H₂CO) on TiO₂(110) and on WO₃ (< 4 x 10¹⁴ WO₃/cm²) on TiO₂(110). On TiO₂(110), H₂CO adsorbs and desorbs molecularly for all coverages. On WO₃/TiO₂(110), the adsorption of H₂CO multilayers results in the catalytic formation of trioxane. The trimerization yield increases with the amount of adsorbed H₂CO and saturates for coverages exceeding ~10 ML. Submonolayer coverage of H₂CO do not yield any trioxane product. The yield increases linearly with the amount of deposited WO₃ and the reaction can be run repeatedly.

@FootnoteText@ *Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am SS2-WeM9 Growth and Reactivity of Palladium Oxide Thin Films, J. Wang, E.I. Altman, Yale University

Palladium has become the catalyst of choice for the catalytic combustion of hydrocarbons in low NO_x gas turbines. Recent studies suggest that oxidized Pd is a more active catalyst for the complete oxidation of hydrocarbons. Our prior work on the oxidation of CO and C₃H₆ on oxygen-covered Pd(100) showed that on the more oxygen rich surface there existed a direct oxidation route for C₃H₆ that proceeds with a lower activation energy than dissociation to C followed by oxidation to CO₂. It was impossible to increase the oxygen coverage much beyond the oxide-like monolayer by dosing with O₂ or NO₂ in UHV. Two approaches are carried out to access the regime where bulk PdO forms: oxidizing the Pd(100) using an oxygen plasma in UHV; and direct growth of PdO thin films. In the first approach, XPS showed that exposure to the plasma at 575 K created bulk PdO, while temperature programmed desorption (TPD) showed an order of magnitude increase in the amount of oxygen compared to NO₂ exposure. The reactivity of C₃H₆ on such surfaces is studied using TPD, isothermal kinetic measurements, and LEED. TPD is used to measure adsorption/reaction kinetics; mass spectroscopy to search for potential reaction products. Isothermal oxygen titration studies are performed by loading oxygen and then exposing to the reductant at fixed temperatures, which yields reaction rates versus oxygen coverage at constant temperatures, repeating the experiments at different temperatures yields activation energies. In the second approach, single crystal PdO(001) films are grown on MgO(100) substrate using oxygen plasma assisted molecular beam epitaxy (OPAMBE). In situ reflection high energy electron diffraction (RHEED) is used to monitor the growth. Ex situ XRD, LEED, XPS and UPS are used to study the bulk and surface orientation, the surface composition and chemical states. The reactivity of the epitaxial films towards C₃H₆ will be compared with that of the poorly ordered PdO formed by oxidizing Pd(100).

11:20am SS2-WeM10 Growth and Catalytic Activity of Epitaxial Palladium(111) Films, Z. Dohnalek, J. Kim, B.D. Kay, Pacific Northwest National Laboratory

Thin Pd films of various thickness were deposited on FeO(111) and Pt(111) substrates at 40 K. The morphology of the resulting films was characterized using low energy electron diffraction, Auger electron spectroscopy, and Kr and CO temperature programmed desorption as a function of annealing. The Pd layers deposited on Pt(111) are stable and develop into a well ordered Pd(111) films at annealing temperatures ranging from 500 to 1000 K. The Pd films deposited on FeO(111) can be ordered by annealing to 500 K but dewet upon heating to higher temperatures. The efficiency of ethylene hydrogenation was examined on these films as a function of their thickness and surface order. As the Pd(111) film thickness is decreased from 100 to 3 monolayers (ML), only a small increase (1 to 2%) in the hydrogenation efficiency is observed. This implies that H diffusion into the bulk does not play an important role for the films in this thickness range. A dramatic increase in the hydrogenation efficiency, resulting in yields up to 50%, occurs on the films covered with a disordered Pd layer (0-2ML) deposited at 40 K suggesting that the hydrogenation reaction is a structure dependent reaction.

@FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:40am SS2-WeM11 Structure-Activity Relationship: The Case of CO and CO₂ Adsorption on ZnO(0001), H/ZnO(0001), Cu/ZnO(0001), J. Wang, S. Funk, B. Hakkanen, E. Johnson, North Dakota State University; U. Burghaus, North Dakota State University, Cass

Molecular beam scattering techniques were combined with thermal desorption spectroscopy (TDS) and applied to a number of different Zn-terminated ZnO systems; namely, clean ZnO(0001), defected ZnO(0001), H precovered ZnO(0001), and Cu precovered ZnO(0001). Furthermore, CO and CO₂ have been used as probe molecules with the goal to address the Structure-Activity Relationship (SAR). The CO₂-TDS curves consist of two distinct structures. By modifying the surface with Ar ion sputtering (more defects) and H-preadsorption (fewer defects), the two TDS structures could be assigned to adsorption of CO₂ on pristine and intrinsic defect sites with binding energies of 34.4 kJ/mol and 43.6 kJ/mol, respectively. Furthermore, He atom reflectivity curves indicated adsorption of CO₂ on defects. Thus, a kinetic SAR is evident. (See, Chemical Physics Letters 403 (2005) 42). Furthermore, a dynamic SAR was present in CO adsorption on the Cu/ZnO(0001) model catalyst. Whereas on small Cu sized-deposits, direct Langmuirian adsorption dynamics were observed; larger cluster sizes lead to the detection of precursor mediated adsorption dynamics of CO. Thus, the energy transfer processes governing the adsorption of a gas phase species on the surface depended distinctly on the morphology of the metal-on-metal oxide system. In the case of CO₂-Cu/ZnO(0001) a strong metal support interaction was observed; TDS and beam scattering data provide consistent hints that CO₂ populates predominantly along the rim of the Cu clusters. Monte Carlo Simulations have been applied for modeling of the molecular beam scattering data.

Surface Science

Room 202 - Session SS+EM-WeA

Organic Film Growth and Characterization

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

2:00pm **SS+EM-WeA1 Comparison of the Electronic Structure of Ferroelectric Polymers**, *J. Xiao, L.G. Rosa, M. Poulsen, D.Q. Feng, S. Ducharme*, University of Nebraska-Lincoln; *P.A. Dowben*, University of Nebraska-Lincoln, US

We compare the electronic structure of copolymers of polyvinylidene fluoride with trifluoroethylene P(VDF-TrFE, 70%:30%) with polymethylvinylidencyanide (PMVC). Crystalline thin films can be formed from both ferroelectric polymers and we find that in both cases the dipole is aligned along the surface normal. The P(VDF-TrFE) copolymer is generally observed to have the chemical potential close to the lowest unoccupied molecular orbital, with a band gap of about 6 eV. PMVC exhibits a much greater band gap, with the Fermi level placed roughly mid way within the highest occupied to lowest unoccupied molecular orbital (HOMO-LUMO) gap. The implications of these differences in electronic properties will be discussed, in particular with regard to electron-phonon coupling.

1@Jaewu Choi, P.A. Dowben, S. Pebley, A. Bune, S. Ducharme, V.M. Fridkin, S.P. Palto, N. Petukhova, Phys. Rev. Lett. 80 (1998) 1328-1331
2@Chun-gang Duan, W.N. Mei, J.R. Hardy, S. Ducharme, J. Choi, P.A. Dowben, Europhys. Lett. 61 (2003) 81-87
3@Luis G. Rosa, Ya.B. Losovij, J. Choi, and P.A. Dowben, J. Physical Chemistry B 109 (2005) 7817-7820.

2:20pm **SS+EM-WeA2 Energetics of Metals Adsorption on Polymers: Calorimetric Studies**, *J.F. Zhu, S.F. Diaz, P. Goetsch, J.J.W. Harris, C.T. Campbell*, University of Washington

We report here the first calorimetric measurement of any metal adsorption energy onto any polymer surfaces wherein the sticking probability of the metal also was measured. The heat of adsorption and sticking probability were measured for Pb and Ca gas atoms adsorbing onto clean poly(methyl methacrylate) (PMMA) and electron-irradiated PMMA. The PMMA film was spin coated directly onto the heat detector, a pyroelectric polymer foil (polyvinylidene fluoride - PVDF) precoated on both sides with metal thin films to serve as electrodes. This provides a detector sensitivity of ~450 V/Jabs with a pulse-to-pulse standard deviation of 1.2 kJ/mol and an absolute accuracy within 2%. The Pb atoms interact very weakly with the outgassed pristine PMMA surface, with a sticking probability of 0.02 ± 0.02 . They deposit a heat into the PMMA of 12.7 ± 0.7 kJ per mole of dosed Pb, independent of Pb exposure up to 10 ML. This is slightly less than would be expected even if no Pb atoms stuck to the PMMA, but if they completely thermally accommodated to the substrate temperature during their collisions with the surface. This proves that thermal accommodation is incomplete, highlighting the weakness of the Pb - PMMA interaction. Calcium interacts with pristine PMMA much more strongly, with an initial sticking probability of ~0.5 and an initial heat of adsorption above 240 kJ/mol. Damaging the PMMA surface with electrons causes an increase in reactivity with Pb, as evidenced by increases in the initial heat of adsorption up to 134.0 ± 0.7 kJ/mol and the initial sticking probability up to 0.51 ± 0.01 . Both increase with increasing coverage toward values expected for Pb adsorption onto bulk Pb.

3:00pm **SS+EM-WeA4 Contrasting the Assembly and Molecular Architecture of N-heteroaromatic Molecular Films on Ag(111): ACA vs. INA**, *H. Li, B. Xu, D. Evans, J. Reutt-Robey*, University of Maryland at College Park

Monolayer films of isonicotinic acid (INA) and 9-acridine carboxylic acid (ACA) were prepared by physical vapor deposition and investigated with complementary scanning tunneling microscopy (STM) and spectroscopy (XPS, RAIRS) under UHV conditions. These N-heteroaromatic acids offer the same H-bonding motifs, but varied sizes and electrostatic properties, which should impact film architecture. In the monolayer regime, STM images reveal that both molecules readily assemble at room temperature into ordered "2-D" structures with typical domain sizes exceeding 100 nm for INA and 1000 nm for ACA. Differences between the domain structures (INA domains being more anisotropic and with much sharper (molecularly smooth) boundaries) are related to differences in their intermolecular forces. We propose structural models consistent with high resolution STM images and test these structural models with detailed spectroscopic

measurements. XPS studies of N 1s and O 1s core level shifts identify a predominant H-bonding motif based upon N head-to- carboxyl tail interaction, in agreement with the proposed structural model. Surface infrared measurements of INA molecular films detect a pronounced out-of-plane aromatic H bending mode at 858 cm⁻¹, and an intensity analysis determines the aromatic plane to be tilted by ~20° from the substrate plane. The proposed structural model for ACA involves an arrangement of ACA molecules with greater and alternating tilt angles, which we are presently testing with infrared experiments. We will account for these distinct molecular film architectures with the differences in the intermolecular forces and discuss the generality of these effects.

3:20pm **SS+EM-WeA5 Intermolecular Interactions in Ultrathin Organic Films**, *N.V. Richardson*, University of St Andrews, UK **INVITED**

Across the complexity of molecular systems, which have now been studied in great detail at well-defined, single crystal surfaces, particularly metal surfaces, there is a great variety in the strength, nature and significance of the intermolecular interactions which are possible. It is the balance of these interactions with the adsorbate/substrate interaction that is a key determinant of the two dimensional order, which can be achieved in the system. In the simplest cases, the interaction may be limited to Van der Waals' attractions balanced by local steric repulsion, while in more complex cases, highly directional H-bonding interactions can dominate the interadsorbate interaction. In the case of adsorption on relatively soft metals such as copper, silver and gold the strength of the interaction of the molecule with the surface atoms can be comparable with or even greater than that between the surface metal atoms, this can lead to the formation of highly ordered 2D adsorbate structures involving significant translocation of metal atoms, most likely in the form of metal adsorbate complexes, and consequential large scale restructuring of the surface. In this presentation, some examples of the relevance of intermolecular interactions in determining adsorbate structures in the sub-monolayer to monolayer regime will be given based on our studies of molecules ranging from aromatic hydrocarbons, through alkane and fluoroalkane thiols to simple biomolecules, such as amino acids and nucleic acid bases. In a somewhat more detailed description of two adsorbate-substrate systems, the role of a two dimensional monolayer in templating a novel three dimensional bulk structure will be described and, in the other example, the ability of a racemic mixture of adsorbing molecules to exploit intermolecular interactions leading to chiral phase segregation will be demonstrated.

4:00pm **SS+EM-WeA7 Conformational Changes and Chiral Ordering in Adsorbed Molecular Layers Investigated by Time-resolved STM**, *S. Weigelt¹, C. Busse, L. Petersen, T.R. Linderoth, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher*, University of Aarhus, Denmark

Detailed understanding of intermolecular interactions and molecular dynamical processes is required to control, and ultimately exploit, molecular self-assembly on surfaces. Recently, self-assembled structures formed from molecules that become chiral once confined to the surface plane have received particular attention. In this contribution we investigate a family of organic molecules that surprisingly can switch chirality as well as switch between chiral and non-chiral forms after adsorption by undergoing spontaneous conformational changes. The molecules (oligo-(phenylene-ethynylene)s) consist of a central benzene ring with two or three ethynylene spokes each terminating in a tert-butyl substituted salicylaldehyde moiety. Upon vapour deposition onto the Au(111) surface under UHV conditions, the molecules assume different surface conformers, distinguishable in STM images by the positions of the tert-butyl groups relative to the molecular backbone. Some of these surface conformers are chiral and the chirality of the conformers and the chirality of the assumed molecular tiling patterns are highly correlated. The correlation is enabled by an intra-molecular switching mechanism, allowing the adsorbed molecules to flip between different surface conformers (and hence between different chiral forms) by rotating their end groups around the axis of the ethynylene spoke. This chiral switching enable the molecules to form extended homo-chiral domains by dynamically accommodating to the chiral template found at domain perimeters. We have performed a detailed investigation of this intra-molecular dynamic process by monitoring the surface with time-resolved STM at substrate temperatures in the interval 150-220K. The rate for the conformational change follows an Arrhenius dependence on temperature with activation energy ~0.3 eV. Theoretical modeling is currently being performed to illuminate this novel intra-molecular dynamical process.

¹ Morton S. Traum Award Finalist

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4:20pm **SS+EM-WeA8 Resonant Soft X-Ray Emission and Inelastic X-Ray Scattering Studies of Electronic Structure in Metal Phthalocyanines**, Y. Zhang, S. Wang, L. Plucinski, Boston University; J.E. Downes, Victoria University of Wellington, New Zealand; C. McGuinness, Trinity College Dublin, Ireland; P.A. Glans, T. Learmonth, K.E. Smith, Boston University

We report synchrotron radiation-excited resonant soft x-ray emission (SXE) spectroscopy and resonant inelastic x-ray scattering (RIXS) studies of the electronic structure of thin films of metal phthalocyanines (M-Pc). SXE measures the element-resolved partial density of states (PDOS) in materials. At a core level resonance, SXE measures the non-ionized PDOS associated with specific chemical sites. Furthermore, RIXS features can be observed which are related to low energy excitations in the system. We discuss the application of SXE and RIXS in the study of M-Pc. Our results are in excellent agreement with theory, but differ significantly from previously published experiments. The films were found to be highly susceptible to beam damage. We successfully circumvented this effect by continuous film translation during measurement. Resonant SXE spectra from undamaged Cu-Pc samples show spectral features near the Fermi level (E_F) that, although predicted, have not previously been observed. We have also studied vanadium oxide phthalocyanine (VO-Pc), and in addition to measuring the element resolved PDOS, have observed dipole forbidden $V\ 3d - V\ 3d^*$ and $O\ 2p - V\ 3d^*$ charge transfer transitions across the band gap. The ability to accurately measure states near E_F is significant, as is the discovery that many SXE studies of organic semiconductors are dominated by beam damage effects. Supported in part by the ACS PRF, by NSF DMR-0304960, and by DOE DE-FG02-98ER45680. The spectrometer system is funded by U.S. ARO DAAD19-01-1-0364 and DAAH04-95-0014. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences. J.E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

4:40pm **SS+EM-WeA9 Effects of Incident Kinetic Energy on the Nucleation and Morphological Evolution of Organic Thin Films**, A.S. Killampalli, T.W. Schroeder, J.R. Engstrom, Cornell University

The deposition and growth of thin films of organic materials differs fundamentally from that of the more conventional inorganic materials. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials, whereas organic materials are often bound by rather weak dispersion forces. As a consequence, considerable promise exists in the use of energy tunable molecular beams for the deposition of organic thin films, as incident species with energies on the order of a few eV may produce substantial changes in the growth habit. We have been examining the deposition of pentacene thin films using a supersonic molecular beam source producing hyperthermal ($E_{\text{subi}} = 1.4 - 10.6\ \text{eV}$) kinetic energies. In both the monolayer and multilayer regimes of growth of pentacene on SiO_2 we find that as E_{subi} is increased from 1.5 to 6.7 eV, the growth rate at a fixed incident flux decreases, consistent with trapping-mediated adsorption. In the monolayer regime the data is well explained by nucleation theory, where the critical island size is 4.5 ± 1.3 . The situation is more complex in the multilayer regime - here the decrease in the rate is less than that observed in the monolayer regime, and at sufficiently large $E_{\text{subi}} (> 4\ \text{eV})$, the rate of deposition in the multilayer regime exceeds that in the monolayer regime by about a factor of 3. The evolution of surface roughness provides additional clues as to the dynamics of growth in the multilayer regime. For all incident kinetic energies, the growth exponent, β , is greater than 0.5, indicative of rapid roughening. Our results demonstrate clearly that the morphological evolution of organic thin films can be modified substantially at high incident kinetic energies.

5:00pm **SS+EM-WeA10 Para-Sexiphenyl Thin Films Grown by Hot Wall Epitaxy on KCl(001) Substrates**, A.Yu. Andreev, A. Montaigne, University Linz, Austria; G. Hlawacek, University of Leoben, Austria; T. Haber, R. Resel, Graz University of Technology, Austria; H. Sitter, University Linz, Austria; C. Teichert, University of Leoben, Austria

Para-sexiphenyl (p-6P) is a blue emitting organic semiconductor widely investigated for optoelectronic applications. Especially, p-6P thin films grown on mica(001) and KCl(001) substrates show large morphological, electrical and optical anisotropy, which makes them attractive for nanoscale optoelectronic and photonic devices. In this work, we use Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) to study the growth of p-6P on crystalline KCl substrates, in order to find the process controlling parameters. It is shown that the growth process of p-6P on KCl(001) is quite complex and can be divided preliminarily in two steps. The initial growth

stage is characterized by the formation of the long needle-like crystallites build of "laying" molecules (as shown by XRD), generating a rectangular network in accordance with substrate surface symmetry. If the surface coverage increases, terraced crystalline mounds composed of upright standing molecules start to develop between the needles. These mounds are clearly formed due to repeated 2D nucleation of p-6P molecules. Consequently, all terraces found are in average about 2.6 nm high, which corresponds to one monolayer of standing p-6P molecules. Further, growth is characterized by a coexistence of the constantly growing needles and mounds, whereby the last ones cover finally almost the whole surface between the needles. By means of phase imaging in AFM tapping mode, it could be clearly demonstrated that both needle-like crystallites and flat terraced mounds grow directly on the substrate surface, i.e., there is no wetting layer formed during the deposition of p-6P on KCl(001).

Surface Science

Room 200 - Session SS1-WeA

Surface Structure and Morphology Modification

Moderator: P.F. Lyman, University of Wisconsin-Milwaukee

2:00pm **SS1-WeA1 Structure and Reactivity of Nanoscale Faceted Surfaces**, T.E. Madey, I. Ermanoski, H. Wang, W. Chen, A.S.Y. Chan, E. Loginova, N.M. Jisrawi, Rutgers University; W. Swiech, University of Illinois at Urbana-Champaign

INVITED

Many planar metal surfaces that are rough on the atomic scale, such as fcc Ir(210), hcp Re(12₃₁), NiAl(111) and bcc W(111), are morphologically unstable when covered by monolayer films of oxygen, or of certain metals: they become "nanotextured" when heated to elevated temperatures. Faceting occurs when an initially planar surface converts to a "hill and valley" structure, exposing new crystal faces of nanometer scale dimensions. Faceting is driven by surface thermodynamics (anisotropy of surface free energy), but controlled by kinetics (diffusion, nucleation). We report here on the relations between structure, reactivity and electronic properties of nanoscale faceted surfaces. Measurements include STM, LEED, TPD, low energy electron microscopy (LEEM) and soft x-ray photoemission (SXPS) using synchrotron radiation. For example, annealing oxygen-covered Re(12₃₁) gives a sequence of faceted surfaces ranging from long sawtooth ridges, to complex structures exposing up to 5 different facets. Surface reactivity of O-covered Re is sensitive to facet structure. Oxygen-faceted NiAl(111) is covered by an alumina "skin". Annealing O-covered Ir(210) generates nanoscale pyramids with {311} and {110} facet orientations; average pyramid sizes 5 to 15 nm are controlled by annealing T. Oxygen can be completely removed at low T (by exposing to $\text{H}_{\text{sub}2}$, to form $\text{H}_{\text{sub}2}\text{O}$) thus creating a clean, faceted surface that is stable to 600K. Faceted Ir is a template for studies of energy-related surface reactions whose rates are sensitive to atomic structure and/or nanoscale (facet) size effects, including decomposition of $\text{H}_{\text{sub}2}$, $\text{C}_{\text{sub}2}$ and $\text{NH}_{\text{sub}3}$. We will discuss structural and electronic properties of the surfaces, nucleation and growth of facets, implications for catalysis, and potential of faceted substrates as nanotemplates for nanoscale cluster growth. Experimental results are compared to theory. Supported by DOE - BES.

2:40pm **SS1-WeA3 Atomistic Reasons for the Oxygen Induced Step Bunching on Rh(553)**, J. Gustafson, A. Resta, A. Mikkelsen, R. Westerstrom, J.N. Andersen, J. Weissenrieder, E. Lundgren, Lund University, Sweden; F. Mittendorfer, G. Kresse, Universität Wien, Austria; X. Torrelles, Institut de Ciencia de Materials de Barcelona (C.S.I.C), Spain; S. Ferrer, ERSF, France; N. Kasper, Max-Planck Institut für Metallforschung, Germany; M. Schmid, P. Varga, Technische Universität Wien, Austria

One of the most fundamental gas-surface interactions is that between oxygen and metal surfaces. Many studies on low index single crystal surfaces have led to an atomic scale understanding of the possible dissociation pathways for the oxygen molecule and the adsorption sites of O-atoms and molecules on such flat surfaces. Oxygen interaction with vicinal surfaces - which due to their high step density better model small metal particles typically used in catalysis - has received much less attention. Similarly only few studies have been performed under conditions - higher temperatures and/or higher oxygen pressures - where strong rearrangements of the substrate surface may occur. Accordingly an atomic level understanding of the oxygen-surface interaction under conditions - material, pressure, and temperature - typical for instance for catalysis is still in its infancy. Here we present an extensive study, using a multi-

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method approach, of the initial oxidation of Rh(553), a surface vicinal to (111) with a large density of steps. Our results show that the surface undergoes step bunching when exposed to oxygen, forming lower index facets. At a pressure of about 10⁻⁶ mbar and a temperature of 400 Å°C this leads to (331) facets with 1D-oxide chains along the steps, co-existing with (111) facets. Increasing the pressure and temperature further results in (111) facets only, covered by a O-Rh-O surface oxide as found on Rh(111).@footnote 1@ @FootnoteText@ @footnote 1@ J. Gustafson et al., Phys. Rev. Lett. 92 (2004) 126102.

3:00pm **SS1-WeA4 Atomic-Scale Visualization of Surface Alloys: Sb/Au(110)**, S.S. Parihar, V.L. Shneerson, R. Fung, H.T. Johnson-Steigleman, E.D. Lu, D.K. Saldin, P.F. Lyman, University of Wisconsin-Milwaukee

Surface x-ray diffraction (SXRD) allows quantitative, high-resolution determinations of surface structure via @chi@ @super 2@ refinement of a model structure to the observed data. However, the most difficult step in this process is often generating model structures to refine. While this is often possible based, e.g., on chemical intuition, a model-independent method of generating accurate starting structures is sorely needed. We have developed an iterative algorithm to supply the phases, normally not accessible to experiment, from data that are oversampled (relative to the Nyquist frequency of the normal dimensions of the selvedge) along the crystal truncation rods. The algorithm alternately satisfies known constraints of these oversampled data in real and reciprocal space, and incorporates knowledge of the bulk structure, to progressively determine the surface structure factor phases. An inverse Fourier transform then constructs an "image" of the atomic contents of a unit cell of the selvedge.@footnote 1@ We have discovered a rich sequence of Sb-induced reconstructions on Au(110). A c(2x2) appears at 0.5 ML, changing continuously to a (@sr 3@x@sr 3@)R54.7° structure at higher Sb coverages; finally, a p(5x6) structure emerges for several ML Sb deposition. We have applied our novel SXRD algorithm to these surfaces to directly visualize the Sb and Au atomic locations, and thereby solve these structures. This breakthrough affords an automated, model-independent method of determining unknown structures of the outermost few atomic layers of a crystal surface. @FootnoteText@ @footnote 1@ P.F. Lyman, V.L. Shneerson, R. Fung, R.J. Harder, E. D. Lu, S.S. Parihar, and D.K. Saldin, Phys. Rev. B 71, 081402(R) (2005).

3:20pm **SS1-WeA5 Adatom-Pair Chain Structures: Metastable Precursors to Island Formation on the Ge-Si(100) 2xN Alloyed Surface**, K.J. Solis, L.R. Williams, University of New Mexico; B.S. Swartzentruber, Sandia National Laboratories; S.M. Han, University of New Mexico

We have identified that adatom pairs are the main transport adspecies on the 2xN SiGe wetting layer, using polarity-dependent scanning tunneling microscopy. These adatom pairs form chevron-like, conjugated chains on the SiGe alloy surface, ranging in length from 1 to approximately 10 units of adatom pairs. The adatom-pair chains exhibit kinked and straight segments. We measure a kink-to-straight ratio of 2:1, surpassing the 1:1 ratio predicted from random chain configurations. Substrate-mediated-strain interactions are likely to render the kinked segments energetically favorable. These adatom-pair chains convert to compact islands at elevated temperatures, suggesting that they are the main precursor to island formation on the SiGe wetting layer. We use a pattern-recognition algorithm to distinguish adatom pairs from compact islands in dual-polarity images, and measure the conversion rate from 90 to 150 °C to extract the activation barrier. The authors acknowledge support from NSF CAREER (DMR-0094145) and ARO (W911NF-05-1-0012). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:40pm **SS1-WeA6 Growth and Subsequent Decomposition Kinetics of Very Thin Oxide on Si(001) Surface Studied by Real-Time RHEED Combined with AES**, S. Ogawa, Y. Takakuwa, IMRAM, Tohoku University, Japan

In order to clarify the rate-limiting reaction of layer-by-layer oxidation on Si surfaces, the growth and subsequent decomposition kinetics of very thin oxide on the Si(001)2x1 surfaces were investigated by a real-time monitoring method of Reflection High Energy Electron Diffraction combined with Auger Electron Spectroscopy (RHEED-AES) to measure the oxide coverage and surface structure/morphology simultaneously. The 1@super st@ oxide layer was grown by two oxidation manners of Langmuir-type adsorption at 500°C and two-dimensional (2D) oxide island growth at 690°C under 2X10@super -6@ Torr of O@sub 2@ pressure. No progress of 2@super nd@ oxide layer growth was observed after

completion of 2D oxide island growth, although the 2@super nd@ oxide layer can grow gradually following the Langmuir-type adsorption. It is difficult to interpret the observed difference in the 2@super nd@ oxide layer growth kinetics, because the observed tendency is contrary to thermal activation from 500°C to 690°C. Furthermore, thermal decomposition of the oxide grown at 690°C is more difficult than that grown at 500°C. Thus the rate of 2@super nd@ oxide layer growth is closely concerned with that of decomposition. The reason for the correlation is quantitatively discussed with the time of void nucleation measured as a function of oxidation time after completion of 1@super st@ oxide layer growth.

4:00pm **SS1-WeA7 Surface Morphologies produced by Oxygen Etching of Stable and Unstable Si Surfaces**, A.A. Baski, M.L. Willis, J.W. Dickinson, J.L. Skrobiszewski, Virginia Commonwealth University

We have used scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to study the morphologies produced on Si surfaces by oxygen etching. When Si surfaces are heated to between 700 and 850°C and exposed to O@sub 2@, the simultaneous processes of etching and oxide nucleation can significantly modify the surface structure. As etching removes surface atoms, oxide-induced pinning sites can modify the step structure and lower-energy facet planes can be exposed. In these experiments, a range of O@sub 2@ exposures (50 to 400 L) have been explored for surface orientations that include: (001), (111), (113), (5 5 12), and (112). All of these orientations except Si(112) form stable, clean surface reconstructions. At lower exposures and temperatures, oxygen etching on all of the surface orientations leads to step retraction and the appearance of islands on terraces and at step edges. These islands are presumably due to oxide-induced pinning sites that remain as the surrounding area is etched. The high-index (113) and (5 5 12) surfaces show significantly less terrace etching and enhanced island nucleation along step edges. At higher exposures and temperatures, fewer kinetic limitations are present and the resulting morphologies reflect the stability of surface planes. The (001), (111), and (113) surfaces remain relatively flat with monolayer islands that reflect the surface symmetry. In contrast, the less thermodynamically stable (5 5 12) surface is etched to expose linear sawtooth structures composed of (111) and (113) planes. Similarly, the unstable (112) surface shows dramatic restructuring with the formation of sawtooths composed of (111), (113), (225), and/or (337) planes. Short (112) segments are also sometimes observed, indicating that adsorbed oxygen may stabilize this otherwise unstable orientation. Further studies are in progress to examine exposures above 1000 L where a steady-state morphology should exist.

4:20pm **SS1-WeA8 Cyclic Transformation of 1-D Structures during Homoepitaxy of Si(5 5 12)-2x1**, H. Kim, Y. Cho, J.M. Seo, Chonbuk National University, Korea

In the homoepitaxy of Si(5 5 12)-2x1 at a finite temperature, 500 C, it has been found by STM that Si overlayer grows in the layer-by-layer fashion and there are three distinct stages, such as dimer-filling, faceting, and valley-filling stages, for recovering Si[5 5 12]-2x1. In each transformed stage, the number of dangling bonds as well as 1-D symmetry with three kinds of reconstructed features, such as honeycomb(H) chain, tetramer(T) row, and dimer-facing-adatoms(D/A) row, are always preserved on the reconstructed surface under a quasi-equilibrium state with deposited Si atoms. The simple rule observed in this 1-D structural transformation is as follows: A honeycomb(H) chain is broken into a tetramer(T) row by the compressive stress, a T row is split to a dimer-facing-adatoms(D/A) row by the tensile stress, and a D/A row is transformed to a H chain by two adsorbed-dimers. Only in the last transformation, the center of 1-D feature shifts in the direction of [-6-6 5] by 3.04 Å. It takes only 28 atoms per unit cell to recover the identical, planar and reconstructed Si(5 5 12)-2x1. The reason why such an amount of Si atoms for recovering the original surface is much smaller than that of surface atoms involving in the reconstruction of Si(5 5 12) is in the fact that the exact growth-direction is not along [5 5 12] but along [-1-1 2]. One-cycle of homoepitaxy is completed when seven (111) double-step edges of a unit-cell of Si(5 5 12)-2x1 are filled with two dimers respectively, and results in the effective height increment of 1.36 Å and horizontal shift of 3.04 Å toward [-6-6 5].

4:40pm **SS1-WeA9 Intrinsic Vacancy-Induced Nanostructure of Al@sub 2@Se@sub 3@: Another New Silicon Compatible Chalcogenide Based Semiconductor**, C.Y. Lu, J.A. Adams, D.A. Schmidt, X. Li, Q. Yu, M.A. Olmstead, F.S. Ohuchi, University of Washington

Adding new functionalities, such as magnetism and spintronics, to existing silicon-based technology requires combining different crystalline materials

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with silicon through heteroepitaxy. One intriguing class of materials that is both structurally and chemically compatible with silicon is the Group-III-Selenide semiconductors, such as Ga@sub x@Se@sub y@ and Al@sub x@Se@sub y@. These materials have intrinsic vacancies that influence the film morphology and resultant crystalline structure during the heteroepitaxial growth, and may also be used to host dissimilar atoms, such as magnetic transition metals, to add unique functionalities. We report here in-situ scanning tunneling microscopy and photoelectron spectroscopy of aluminum-selenide (Al@sub x@Se@sub y@) heteroepitaxy on Si(111)-7x7 and As-terminated Si(100). Unlike Ga@sub x@Se@sub y@, which crystallizes into either a layered GaSe or defected zinc-blende Ga@sub 2@Se@sub 3@, Al@sub x@Se@sub y@ exhibits only one bulk structure: defected wurtzite. We find heteroepitaxy of Al@sub x@Se@sub y@ on Si(111) results in hexagonal Al@sub 2@Se@sub 3@, likely wurtzite, but defected zinc-blende Al@sub 2@Se@sub 3@ is initially formed on As-terminated Si(100). The morphology of Al@sub 2@Se@sub 3@/Si(111) consists of triangular nanodots with single orientation, in contrast to the mixed orientation of layered GaSe on Si(111). For Al@sub 2@Se@sub 3@/Si(100):As, we observe oriented nanowire structures at low coverage, similar to low coverage Ga@sub 2@Se@sub 3@/As:Si(100)nanowires;@footnote 1@ hexagonal crystalline islands nucleate after 2-3 bilayers. In these first 2-3 layers, the spiral vacancy arrangement unique to the wurtzite structure is altered to a linear array by the symmetry of Si(100)substrate. We propose that different symmetry and bonding of the substrate surfaces induces different configurations of vacancies, resulting in the distinct surface nanostructures. @FootnoteText@ @footnote 1@T. Ohta et al., Phys. Rev. Lett. 94, 116102 (2005).

Surface Science

Room 203 - Session SS2-WeA

Reactions on Nanoclusters

Moderator: I. Chorkendorff, Technical University of Denmark

2:00pm **SS2-WeA1 Physical and Chemical Properties of Model Catalysts Prepared by Size-Selected Cluster Deposition**, *T. Wu, S. Lee, C. Fan, W. Kaden, S.L. Anderson*, University of Utah

In surface chemistry, one of the most important goals is to understand the relationship between surface structure and catalyst reactivity, especially at an atomic level. An interesting aspect of this field is the effect of particle size in supported catalysts, i.e., how cluster size affects the physical properties of the surface, as well as the activity for specific reactions. In our lab, model gold, iridium, and palladium catalysts were prepared by deposition of size-selected metal clusters on well defined oxide surfaces, and characterized by a combination of X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), temperature-programmed desorption, and pulse-dosing mass spectrometry. Activity is strongly size-dependent. For example, in reaction of hydrazine on Ir/alumina model catalysts, both activity, and the distribution of products change dramatically with cluster size. Strong dependence on size is also seen for CO oxidation.

2:20pm **SS2-WeA2 Probing the Chemical Reactivity of Oxide-Supported Pd Nanoparticles with STM**, *J. Zhou, A.P. Baddorf, S.V. Kalinin, S.H. Overbury, D.R. Mullins*, Oak Ridge National Laboratory

Oxide-supported metal nanoparticles play a central role in current heterogeneous catalysis. They may exhibit unique catalytic properties that can be tuned by particle size and structure as well as by choice of oxide substrate. However, there is still a need to understand the origins of catalytic activity of metal/metal-oxide interfaces at the atomic scale. We report scanning tunneling microscopy (STM) studies of supported Pd nanoparticles evaporated on a rutile TiO@sub 2@ (110) single crystal surface in ultrahigh vacuum as a model catalytic system. A range of particle sizes with narrow size distributions was prepared by varying Pd coverage, substrate growth and post-annealing temperatures. Electronic properties of the particles and adjacent substrate were determined with I-V and dI/dV spectroscopies. The surface chemistry of supported Pd particles was explored for reactive gases such as O@sub 2@, CO and benzene between 20 and 300 K. Images of specific particles are compared before and after in situ exposures. Research was sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC for the U. S. DOE under Contract DE-AC05-00OR22725.

2:40pm **SS2-WeA3 Structure and Reactivity of Metal Clusters**, *H.J. Freund*, Fritz-Haber-Institute of the Max-Planck-Society, Germany

INVITED

Model catalyst systems have been prepared by growth of metal nanoaggregates on thin well-ordered oxide films of alumina and silica. These systems lend themselves to structural and morphological characterization via scanning probe microscopies and transmission electron microscopy and bridge to a certain extent the materials gap between metal single crystal studies and the investigation of real catalyst samples. It is possible to infer direct structure-reactivity relations when simple reactions of small molecules are studied. We have applied a variety of surface sensitive techniques, both under ultrahigh vacuum as well as under ambient conditions to relate observations from surface science to those in catalysis under realistic gas pressure conditions. Examples are presented.

3:20pm **SS2-WeA5 The Active Structure of Supported Au Catalysts**, *M.S. Chen, Z. Yan, Y. Cai, W.T. Wallace, X.F. Lai, D.W. Goodman*, Texas A&M University

The high catalytic activity of gold clusters on oxides has been attributed to structural effects, including particle thickness and shape, metal oxidation state, as well as support effects. The best catalytic performance of supported Au particles was found for clusters with sizes of 2~3 nm. For Au clusters supported on TiO2(110), the unique properties have been associated with Au structures two atomic layers in thickness based on STM and kinetic measurements (M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998)), and confirmed by our recent results. Specifically, we have synthesized well-ordered Au monolayers [(1x1)] and bilayers [(1x3)] that completely wet (cover) the oxide support [a titanium oxide monolayer film grown on the Mo(112) surface] (M. S. Chen, D. W. Goodman, Science 306 (2004) 252.). Kinetic measurements for CO catalytic oxidation show that the Au bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer structure, and is approximately 45 times higher than that reported for the most active high-surface-area Au/TiO2 catalysts. These specific rates clearly indicate that bilayer Au is the active structure for CO oxidation. These results eliminate particle shape and direct support effects as significant contributions to the special catalytic properties of nano-sized Au clusters.

3:40pm **SS2-WeA6 Neutralization of Low Energy Li Ions Scattered from Au Nanoclusters**, *G.F. Liu*, University of California, Riverside; *Z. Sroubek*, Czech Academy of Sciences; *J.A. Yarmoff*, University of California, Riverside

Charge exchange during the scattering of low energy (0.5-10 keV) alkali ions provides a sensitive measure of the confined quantum states of nanomaterials. In earlier work, we showed that the neutralization of Na@super +@ scattered from Au nanoclusters correlates with the presence and position of the confined states.@footnote 1@ In this work, we scatter Li ions from Au nanoclusters grown on TiO@sub 2@(110). The neutralization probability of the Li singly scattered from the Au nanoclusters is measured with time-of-flight spectroscopy. Au nanocrystals grown on TiO@sub 2@(110) possess unique catalytic properties, which depend on the cluster size. The size of the clusters is determined by the amount of Au deposited and the surface temperature, and increases with the amount deposited. The neutral fraction was found to have a maximum at ~0.2 ML Au coverage, which is consistent with the maximum seen for the catalytic activity.@footnote 2@ This provides clear evidence that the ion scattering is probing the same states that are responsible for unique properties of these materials. When additional Au is deposited, the neutral fraction first drops to a minimum (at ~10 ML Au), and then increases to the bulk Au value. This shows that ion scattering is able to monitor the formation of the conduction band as a transition is made from isolated clusters to a continuous film. In addition, the dependence of the neutral fraction on the ion exit angle and energy was investigated. In order to better correlate the dependence of the cluster sizes on the neutral fraction, future experiments will involve Li and Na ions scattered from size-uniform nanoclusters grown by chemical synthesis. @FootnoteText@ @footnote 1@G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004). @footnote 2@M. Valden, X. Lai, and D.W. Goodman, Science 281, 1647 (1998).

4:00pm **SS2-WeA7 Growth and Reactivity of Bimetallic Pt-Rh Nanoclusters on Titanium Dioxide**, *S. Ma*, Brookhaven National Laboratory; *J.S. Ratliff, J.B. Park, D.A. Chen*, University of South Carolina

Bimetallic Pt-Rh nanoclusters have been grown on rutile TiO@sub 2@ by vapor deposition under ultrahigh vacuum conditions. Low energy ion scattering (LEIS) experiments show that Pt tends to segregate to the surface of the nanoclusters, regardless of whether Rh is deposited on top of Pt or Pt is deposited on top of Rh. Pt diffusion into the clusters occurs

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readily at room temperature and is only slightly slower when the deposition temperature is decreased to 220 K. Scanning tunneling microscopy (STM) experiments indicate that for 2 monolayers of Pt deposited on 2 monolayers of Rh, the resulting clusters have an average height of 0.9 nm and diameter of 5 nm. Although heating to 850 K significantly increases the Pt-Rh cluster size (1.3 nm height, 7 nm diameter), LEIS experiments indicate that the clusters become completely encapsulated with TiO₂ at temperatures above 700 K. In situ STM experiments demonstrate that during the deposition of Pt on Rh clusters, existing clusters grow bigger, new Pt clusters are nucleated, and many growing Pt-Rh clusters merge with neighbors to form larger clusters. The reaction of NO on pure Pt or Rh clusters results in production of N₂ as well as desorption of NO. However, NO chemistry on bimetallic Pt-Rh clusters is qualitatively different since a new product, N₂O, is also observed. The reduction of NO with CO to produce N₂ and CO₂ does not occur on pure Pt or Rh clusters but is observed on the bimetallic Pt-Rh clusters.

4:20pm SS2-WeA8 Reactive-Layer-Assisted Deposition (RLAD) of TiO₂ Nanoparticles on Au(111) Studied by STM and XPS, Z. Song, Columbia University; J. Hrbek, Brookhaven National Laboratory; R.M. Osgood, Columbia University

TiO₂ nanoparticles have been prepared by reactive-layer-assisted deposition (RLAD), in which Ti atoms are initially deposited on a multilayer of H₂O (or NO₂) grown on a Au(111) substrate at temperature <100 K. The chemical, structural and electronic properties of these oxide nanoparticles were studied by XPS, STM and STS. Specifically, ~1nm diameter TiO₂ particles formed with an H₂O reactive layer were obtained after raising the substrate temperature to 300K. Use of NO₂ reactive layers yields TiO₂ nanoparticles (~1nm at 300K) with NO₃ radicals decorating their surfaces at temperatures below 500K. Further annealing induces the desorption of N-containing species and leaves behind flat TiO₂ rutile and anatase particles (~5nm after being annealed to 700K) with various facets. STS studies showed different electronic structures for different TiO₂ particle sizes. This UHV compatible method for preparing well-defined TiO₂ nanoparticles can be used in molecular-level studies of reaction mechanisms of photocatalytic processes on TiO₂ nanoparticle surfaces.

5:00pm SS2-WeA10 Bimodal Pd Cluster Growth on the Reduced SnO₂ (101) Surface, Kh. Katsiev, M. Batzill, U. Diebold, Tulane University

Tin oxide is a solid state gas sensor for detection of combustible and toxic gases. Its sensitivity and selectivity can be enhanced by catalytically active dopants, such as Pd. We have studied the growth of Pd on the SnO₂ (101) surface in the sub-monolayer regime in order to gain new insights into the gas sensing mechanism. The SnO₂ substrate exhibits a 1x1 bulk termination, with the surface tin atoms in a reduced Sn²⁺ charge state. This reduction of the surface Sn atoms results in the formation of a Sn-5s derived surface state. Upon deposition of Pd onto SnO₂ (101), bimodal cluster growth was observed. For very low coverages, two-dimensional, round clusters decorate (0-10) -oriented step-edges, a behavior typical for many metal-on-oxide systems. In addition, we observe quasi one-dimensional Pd clusters growing on terraces. In both cases Pd wets the reduced tin oxide surface. The one-dimensional clusters are imaged in scanning tunneling microscopy as straight, parallel nanostructures oriented along the (-101) direction, all with the same characteristic width of 1 nm and a height of 1ML. XPS shows metallic Pd. A 0.45 eV shift in the Pd 3d core level peak position to lower binding energy occurs during the initial stages of the growth. This might be an indication of charge transfer from the Pd clusters to the substrate. Coverage-dependent UPS show that at fractional monolayer coverages, a Pd peak appears at the same position in the band gap as the Sn-5s surface state of reduced SnO₂(101), indicating a possible hybridization of Sn-5s with the Pd d-band. This is the first observation of formation of one-dimensional, metallic nanowires on a wide-band gap material.

Surface Science

Room 200 - Session SS1-ThM

Water-Surface Interactions

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

8:20am **SS1-ThM1 Metal/Electrolyte Interfaces: In-situ Scanning Tunneling Microscopy Studies**, *K. Wandelt*, University of Bonn, Germany
INVITED

In the years to come more and more processes at solid/liquid interfaces will replace processes which nowadays are carried out by vacuum based methods, like surface modification, thin film growth, nanostructuring, etc.. Among others this is a consequence of the growing number of methods which are capable to provide in-situ information about properties and processes at solid/liquid interfaces with the same precision as we are used to in vacuum. This is particularly true for ElectroChemical Scanning Tunneling Microscopy (ECSTM), which - in combination with in-situ FTIR- and some ex-situ spectroscopies - is used in this work to characterize copper single crystal electrodes interacting with various electrolytes. Firstly, surface structural phase transitions and morphological changes due to the adsorption of simple anions, like Cl, Br, J, S, SO₄²⁻, SCN, etc., will be studied with atomic resolution. Secondly, it will be shown that the halogen and sulphur covered electrode surfaces are interesting primary templates for the formation of thin ordered compound films (e.g. CdCl₂) as well as self-assembled organic nanostructures (e.g. from porphyrins and viologenes). In particular the latter ones are found to form chiral cavitands, which in turn are ideal secondary templates for the design of more complex molecular architectures with nanoscale periodicity and specific functionality.

9:00am **SS1-ThM3 Segregation of Anions at the Alkali Halide Solution/Vapor Interface Investigated by Photoemission Spectroscopy**, *S. Ghosal*, University of California, Irvine; *H. Bluhm*, Lawrence Berkeley National Laboratory; *B.S. Mun*, Lawrence Berkeley National Laboratory, US; *G. Ketteler*, *F.G. Requejo*, *E.L.D. Hebenstreit*, *D.F. Ogletree*, *M. Salmeron*, Lawrence Berkeley National Laboratory; *J.C. Hemminger*, University of California, Irvine

Ion-enhanced interactions with gases at aqueous solution interfaces may play an important role in the chemistry of concentrated inorganic solutions in the atmosphere. Using ambient pressure photoemission spectroscopy (PES) we have measured the concentration of ions at the surface of saturated potassium iodide and potassium bromide solutions. In the case of saturated potassium iodide solutions two iodine 4d peaks that are separated by a binding energy difference of 1.7 eV can be identified in the PES spectrum. Using photon-energy-dependent depth-profiling we have determined that the iodine peak with the higher binding energy is due to an iodine species at the solution interface, while the low binding energy peak is due to iodine from the bulk of the solution. The presence of an anion species at the solution interface is in agreement with our previous ambient pressure PES results that showed an enhancement of the halide anion concentration at the solution interface compared to the literature value for bulk solutions. @footnote 1@ @FootnoteText@ @footnote 1@ S. Ghosal et al., Science 307, 563 (2005).

9:20am **SS1-ThM4 The Growth of Thin Water Films on a Hydrophobic Water Monolayer on Pt(111)**, *G.A. Kimmel*, *N.G. Petrik*, *Z. Dohnalek*, *B.D. Kay*, Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on Pt(111) is investigated using rare gas physisorption. For a wide range of growth temperatures (20 - 155 K), the water monolayer wets the Pt(111). However, crystalline ice films grown on the water monolayer do not wet that surface. In contrast, amorphous films grow layer-by-layer for at least the first three layers over a wide range of growth temperatures (20-120 K), probably due to kinetic limitations. Wetting films grown at low temperature that are subsequently annealed to high temperature typically unwet during or after the crystallization of the films. The results are surprising since it is commonly believed that water films wet Pt(111). However, they are consistent with recent theory and experiments suggesting that the molecules in the water monolayer are fully coordinated forming a hydrophobic surface with no dangling OH bonds or lone pair electrons and a low surface energy.

9:40am **SS1-ThM5 The Nature of Water on Oxygen Covered Pt: Low Temperature Activation and Unexpected Structure**, *T. Schiros*, *H. Ogasawara*, Stanford Synchrotron Radiation Laboratory; *L.-Å. Näslund*, *M. Odellius*, *L.G.M. Pettersson*, Stockholm University, Sweden; *A. Nilsson*, Stanford Synchrotron Radiation Laboratory

The nature of the adsorbed water layer on surfaces has been a topic of interest due to its relevance for many practical fields, including corrosion, electrochemistry, environmental science and heterogeneous catalysis. Recently the behavior of adsorbed water under the presence of oxygen has garnered increasing interest in connection to the triple phase boundaries problem in fuel cell catalysis. Here, we studied the co-adsorption of water and oxygen on Pt(111) with X-ray photoemission and X-ray absorption spectroscopy in an ultra high vacuum environment combined with electronic structure calculations in the frame work of density functional theory. While water absorbs intact on clean metal surfaces at low temperature, @footnote 1-3@ an oxidized Pt surface activates and splits adsorbed water even at low temperature. We propose a new structure model for the activated water on Pt(111). We find that the activated water aligns the molecular axis perpendicular to the surface and is hydrated in the equatorial plane. @FootnoteText@ @footnote 1@ H. Ogasawara et al, Phys. Rev. Lett. 89 (2002) 276102. @footnote 2@ K. Andersson et al, Phys. Rev. Lett. 93 (2004) 196101. @footnote 3@ K. Andersson et al, Surf. Sci. Lett. In press (2005).

10:00am **SS1-ThM6 DFT Calculations of Interaction of Water Molecules with Pt(111) Surface**, *L. Árnadóttir*, University of Washington; *H. Jónsson*, University of Iceland; *E.M. Stuve*, University of Washington

The interaction of water molecules with the Pt(111) surface has been studied using DFT and the PW91 functional. Early stages of ice crystal nucleation and the possibility of dissociation on flat terrace, kink and steps have in particular been addressed. In the lowest energy configuration, a water molecule sits on top of a Pt atom and donates an electron pair into an empty d-orbital on the Pt. The binding energy is found to be 0.30 eV. Small water clusters of two and three water molecules also have lowest energy configuration on top of a Pt atom. In those small clusters one water molecule is centered on the top of a Pt surface atom and is tilted with the hydrogen atoms pointing about 16° away from the surface plane and the other water molecules about 0.5 Å further away from the surface. While the dissociation of water molecules is uphill by 0.72 eV on the flat terrace, it is almost neutral energetically at the step but has an activation energy of 0.91 eV. The dissociation will, however, not occur thermally because desorption will occur more readily. As the temperature is raised, the diffusion of single water molecule is predicted to become active on the time scale of seconds at a temperature of 43 K which is in good agreement with recent experimental results of Kay and coworkers. @footnote 1@. The binding at steps and kinks on the Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively, and the lowest energy configuration has the water molecule sitting on top of edge or kink atoms. At low coverage, clusters of water molecules would, therefore, be expected to line the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. @footnote 2@ @FootnoteText@ @footnote 1@ Daschbach, J. L., Peden, B. M., Smith, R. S., Kay, B. D., J. Chem. Phys., 2004. 120(3): p. 1516-1523 @footnote 2@ Morgenstern, M., Michely, T., Comsa, G., Phys. Rev. Lett., 1996. 77(4): p. 703-706

10:20am **SS1-ThM7 The Effect of Incident Collision Energy on the Phase, Crystallization Kinetics, and Porosity of Vapor Deposited Amorphous Solid Water Films**, *T. Zubkov*, *R.S. Smith*, *Z. Dohnálek*, *B.D. Kay*, Pacific Northwest National Laboratory

Molecular beam techniques that allow for the precise control of the impingement flux, deposition angle, and incident collision energy are used to grow nanoscale films of amorphous solid water (ASW). The phase (amorphous or crystalline), porosity, and subsequent crystallization kinetics of the ASW films are probed using temperature programmed desorption, inert gas physisorption, and infrared spectroscopy. We find that for films grown at 20 K and normal incidence, the incident collision energy (up to 2 eV) has no effect on the phase of the deposited film or the subsequent crystallization kinetics. On the other hand, the incident beam energy does affect the porosity of the deposited films. At low beam energy (0.05 eV), the porosity of the vapor deposited film depends strongly on the incident growth angle. Films with structures from non-porous to highly porous can be grown by increasing the angle of incidence of the impinging molecules. The porosity of the ASW films decrease with increasing beam energy. The results of these experiments and their implications for the physical

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properties of ASW are presented and discussed. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

10:40am **SS1-ThM8 Ionization of Water-Ice Layers on Platinum: Effect of Carbon Monoxide**, *R.A. Manghani, V.K. Medvedev, E.M. Stuve*, University of Washington

Field ionization of water on a platinum field emission tip was studied in the presence of carbon monoxide (CO) as co-adsorbate. Water adlayers 5 - 400 Å thick were grown under field-free conditions at 108 K by exposure of cryogenically cooled emitter tip to water vapor in ultrahigh vacuum. Onset of field ionization of water layers was probed by ramped field desorption (RFD) on platinum and CO saturated platinum emission tip. Onset field for water ionization on CO saturated platinum was found to be lower than that for water adsorbed on bare platinum. Facilitation of ionization by saturated CO on platinum was attributed to enhancement in the local field. The effect decreased with increasing water thickness, but existed for thick water layers. Effect of CO on water ionization is discussed and a model is presented.

11:00am **SS1-ThM9 Electron-Stimulated Production of Molecular Oxygen in Thin Films of Amorphous Solid Water on Pt(111)**, *N.G. Petrik*, Pacific Northwest National Laboratory; *A.G. Kavetsky*, Khlopin Radium Institute, Russia; *G.A. Kimmel*, Pacific Northwest National Laboratory

The electron-stimulated reactions in amorphous solid water (ASW) films leading to the production of molecular oxygen were investigated. Thin (0-400 ML) amorphous films of H@sub 2@@super 16@O, H@sub 2@@super 18@O, and D@sub 2@O deposited on Pt(111) were irradiated with 87 eV electrons, and the electron-stimulated desorption (ESD) of O@sub 2@ was measured versus film thickness and isotopic composition. The O@sub 2@ ESD yield is low for small coverages, has a maximum at ~20 ML, and decreases to a coverage independent level for coverages greater than ~50 ML. The O@sub 2@ and H@sub 2@ ESD yields versus ASW coverage are similar, indicating that both originate from mobile electronic excitations produced in the bulk of the ASW film that subsequently diffuse to the ASW/Pt and ASW/vacuum interfaces where they induce reactions. However in contrast to H@sub 2@, experiments with layered films of H@sub 2@@super 16@O and H@sub 2@@super 18@O show that O@sub 2@ is produced only near the ASW/vacuum interface. The O@sub 2@ molecule is produced via a relatively fast radiation-induced process from a stable precursor, perhaps HO@sub 2@ or H@sub 2@O@sub 2@, which accumulates at the ASW/vacuum interface. The results suggest that mobile electronic excitations produce a reactive species at the ASW/Pt interface, such as OH, which subsequently diffuses through the film to the ASW/vacuum interface where further reactions produce the stable precursors for the O@sub 2@ molecules.

11:20am **SS1-ThM10 A Comparison of H@sub 2@O and D@sub 2@O Adsorption on MgO(100) Under Ambient Conditions**, *M.C. Foster, N.J. Ward, D. Passno*, University of Massachusetts - Boston

Transmission Fourier transform infrared spectroscopy is used to investigate both H@sub 2@O and D@sub 2@O adsorbed on the (100) face of MgO under ambient conditions. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. Water is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. From these measurements, we find that water reversibly adsorbs to MgO(100) creating liquid-like layers at room temperature with slight hysteresis seen during a complete adsorption / desorption cycle. The adsorption isotherm of water on MgO(100) resembles a typical BET plot, which coupled with by the fact that IR absorption due to either the OH or OD stretch of the adsorbed water does not change as a function of coverage, suggests that the layer grows in via three-dimensional island formation. Special attention has been paid to the issue of dissociative adsorption of water on the surface, either reversible or permanent with no evidence seen under these experimental conditions.

11:40am **SS1-ThM11 Water Adsorption on a Polymer Surface**, *L.G. Rosa¹*, University of Nebraska-Lincoln; *Ya.B. Losovyj*, Louisiana State University; *I.N. Yakovkin*, Institute of Physics of National Academy of Sciences of Ukraine; *P.A. Dowben*, University of Nebraska-Lincoln, US

Water absorption and adsorption on the thin films of the ferroelectric copolymer polyvinylidene fluoride with 30% trifluoroethylene, P(VDF-TrFE,70:30) has been explored by angle resolved thermal desorption, angle resolved photoemission spectroscopy, high resolution photoemission spectroscopy and x-ray diffraction. We observe that water is absorbed into the polymer bulk. When the near surface region is saturated, an ice layer at the surface of the polymer can be formed. Strong dipole - dipole interactions between the dipole of water and the dipole of the ferroelectric polymer play an important role in absorption and desorption, including but not limited to, isotopic exchange and dielectric properties. Adsorbed water seems to be a spectator to the many phase transition of the ferroelectric polymer particularly the ones at the surface and bulk.

Surface Science

Room 202 - Session SS2-ThM

Functionalization of Semiconductor Surfaces

Moderator: J.E. Crowell, University of California, San Diego

8:20am **SS2-ThM1 Dissociative Chemisorption of SiH@sub 4@ on Si(100): Threshold Energy and Mechanism**, *H.L. Abbott²*, University of Virginia; *D.F. Kavulak*, University of California, Berkeley; *I. Harrison*, University of Virginia
A three-parameter local hot spot model of gas-surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH@sub 4@ incident on Si(100) under varied nonequilibrium conditions. Two Si surface oscillators and the molecular vibrations, rotations, and translational energy directed along the local surface normal are active degrees of freedom in the 15 dimensional microcanonical kinetics. The threshold energy for SiH@sub 4@ dissociative chemisorption is found to be 19 kJ/mol, in quantitative agreement with recent GGA-DFT calculations that predict an intra-dimer mechanism. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH@sub 4@ at low surface temperatures and/or on hydrogen passivated Si(100) is discussed.

8:40am **SS2-ThM2 Organic Functionalization of Semiconductors Using Amino Acids; Quantum Resonance Coupling and Electron Transport Effects**, *G.D. Guillaume, G. Zhang, C.B. Musgrave*, Stanford University

We have used DFT to simulate the attachment of amino acids and various unique organic molecules on Si and Ge surfaces. These structures have potential applications in molecular electronics and sensors if their structures can be controlled and if the resulting interface electronic structure provides appropriate electronic properties. We will present a summary of the various unique reactions of amino acids on Si(100)-2x1 we have investigated and focus on certain organics functionalities that are stabilized on Si and Ge by quantum mechanical resonance which stabilize the product and leads to stronger electronic coupling between the attached organic and the semiconductor substrate which might be useful in improving electrode-molecule charge transfer for organic-semiconductor molecular electronic devices. We will also discuss the accurate simulation of the electronic band structure of these molecular junctions required for correct prediction of the electron transport across these junctions. We have found that the common DFT methods are inadequate for this task, although the KMLYP method correctly predicts the HOMO and time-dependent KMLYP (TD-KMLYP) correctly predicts the LUMO energy.

9:00am **SS2-ThM3 Amide Chemistry at the Ge(100)-2x1 Interface**, *A.J. Keung, M.A. Filler*, Stanford University; *S.F. Bent*, Stanford University, US

Organic functionalization of semiconductor surfaces has many potential applications including semiconductor processing, molecular electronics, and chemical sensors. In particular, understanding the surface reactivity of the amide linkage could be important in developing biologically-based devices. In situ vibrational spectra were obtained as a function of coverage, temperature, and time for a series of primary, secondary, and tertiary amides adsorbed on the Ge(100)-2x1 surface under ultrahigh vacuum conditions. For the tertiary amides, including dimethyl formamide, 1-methyl-2-pyrrolidinone, and *n,n*-dimethyl acetamide, asymmetric and symmetric N-C-O stretching, aldehydic C-H bending, as well as methyl deformation modes were observed, while Ge-H stretching modes were

¹ Morton S. Traum Award Finalist

² Morton S. Traum Award Finalist

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absent. This data provides evidence that tertiary amides form a dative-bond between the carbonyl oxygen and the electrophilic germanium dimer atom. Theoretical spectra of dative-bonded structures, calculated with density functional theory, agree well with experiment. In addition, these products desorbed at 310K on the timescale of minutes suggesting dative-bonded tertiary amides are just at the cusp of stability on Ge(100)-2x1. The primary and secondary amides, formamide and n-methyl formamide, respectively, were also investigated. Two types of products were observed for each compound at room temperature. Comparison to the experimental spectra of dimethyl formamide provides evidence for dative-bonded products. Dissociation products were also formed as evidenced by the growth of Ge-H stretches. The dissociation products were favored at higher temperatures, and there is evidence for dative-bonded adducts converting to these products upon annealing. Due to a kinetic barrier to this reaction, the dative-bonded state can be isolated at low temperature. These results have implications for understanding the reactivity of larger biological molecules such as peptides.

9:20am **SS2-ThM4 Layer-by-Layer Growth on Ge(100) via Spontaneous Chemical Reaction**, A. Kim, Korea Advanced Institute of Science and Technology (KAIST), Korea; M.A. Filler, Stanford University; S.F. Bent, Stanford University, US; S. Kim, KAIST, Korea, South Korea

We have demonstrated the layer-by-layer growth, via a urea coupling reaction between two bifunctional molecules, ethylene diamine and 1,4-phenylene diisocyanate, to form an ultrathin film on Ge(100)-2x1 at room temperature under vacuum conditions. The initial adsorption and subsequent growth of each layer was studied with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. Ethylene diamine reacts with Ge(100)-2x1 to produce a surface-bound amine group which is available for additional reaction. Subsequent exposure of 1,4 phenylene diisocyanate leads to a spontaneous urea coupling reaction between the surface-bound amine and highly reactive isocyanate functional group. Three bands at 1665, 1512, and 1306 cm⁻¹ are characteristic of a urea linkage and provide evidence of the coupling reaction. The coupling procedure can be repeated in a binary fashion to create covalently bound ultrathin films at room temperature and, in the present work, we demonstrate the successful growth of four layers. In addition, we have found that an initial exposure of 1,4-phenylene diisocyanate to Ge(100)-2x1 produces an isocyanate-functionalized surface which, upon exposure to ethylene diamine, also forms urea linkages. This layer-by-layer deposition method provides a strategy with which to design and produce precisely tailored organic materials. * Work supported by the Natural Sciences and Engineering Research Council of Canada.

9:40am **SS2-ThM5 Alkylation of Silicon and Germanium Surfaces**, S. Rivillon, Y.J. Chabal, Rutgers University

Chemical modification of semiconductor surfaces is used to modify the surface properties and to provide new functionality. In particular, the formation of self-assembled monolayers (SAM) can lead to a broad range of applications such as micromechanical systems (MEMS), biosensors, lithography, and growth of alternative dielectrics without an interfacial oxide. To date, most work has been performed on silicon surfaces for which wet chemical cleaning methods have been well developed. In this talk, we focus on the alkylation of H- and Cl-terminated Ge surfaces, with close comparison to results of similar treatments on Si surfaces. Using infrared absorption (IR) spectroscopy, we have shown that while HF-etched Si(100) and Ge(100) are atomically rough, the distribution of hydride species is different: hydrogen-terminated Si(100) exhibits mono-, di- and tri-hydride species, while H-Ge(100) only exhibit Ge-H and Ge-H₂ species. The stability of both semiconductor surfaces to air is also different: for H-Si(100), oxygen is slowly incorporated into the substrate, forming O₃-Si-H; for H-Ge(100), little oxidation takes place. Instead, hydrocarbons react with the hydrogen forming Ge-CH₂ species. This propensity of the Ge surfaces for alkylation has been used and comparison with silicon indicates that methoxylation takes place more rapidly on Ge surfaces.

10:00am **SS2-ThM6 Correlation of Surface Electronic Structure with Organic Reactivity on Si(114)**, D.E. Barlow, A.R. Laracuente, L.J. Whitman, J.N. Russell, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5° between (001) and (111). The equilibrium surface reconstruction is comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction. The different Si(114) structural motifs within each row have distinct electronic

structures, making this surface an ideal template for studying the relationship between adsorption site geometry (including symmetry), local electronic structure, and chemisorption of organic molecules on clean silicon surfaces. In this study, we have experimentally characterized the effects of charge transfer, π bonding, orbital symmetry, and di-radical reaction pathways on the cycloaddition chemisorption of ethylene on Si(114)-(2x1). Transmission FTIR spectroscopy was used to confirm the basic chemical structure and orientation of the chemisorbed ethylene. The results indicate a σ bonded product with a C-C bond axis preferentially oriented along the row direction. Using atomic-resolution STM, we identified three common adsorption structures located at the dimer, rebonded atom, and tetramer sites. In correlation with the FTIR results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of site reactivity is found to be rebonded atoms > dimers > tetramers. Reasons for this reactivity trend will be discussed.

10:20am **SS2-ThM7 Contact Formation with a Single Molecule: 1,3-cyclohexadiene on the Si(100) Surface**, B. Naydenov, L.C. Teague, P. Ryan, J.J. Boland, Trinity College Dublin, Ireland

INVITED
We have studied the contact formed between a 1,3-cyclohexadiene (1,3-CHD) molecule on Si(100) and a Pt STM probe tip at 5 K. DFT studies indicate that the STM images obtained are the result of a specific probe-molecule interaction. This is confirmed by measurements of local barrier heights acquired at different probe-molecule separations and the associated change in the vibrational spectra measured at each separation. On this basis, we provide a detailed analysis of the physical and chemical interactions that accompany contact formation in this molecular system.

11:00am **SS2-ThM9 Surface Functionalization of Si(100)2x1 by Halogenated Ethylenes: Formation of C2-dimer, Vinylene, Vinylidene, and their Halogenated Derivatives**, K.T. Leung, X.J. Zhou, University of Waterloo, Canada

Our recent studies on halogenated ethylenes on Si(111)7x7 and Si(100)2x1 have demonstrated the importance of a competing insertion mechanism to the commonly observed cycloaddition mechanism for Si surface functionalization. The combination of the C=C bond with Cl atoms provides interesting molecular platforms for investigating various novel effects involving different molecular symmetries and structures, Cl content and structural chemistries. The adsorption of these chlorinated ethylenes and their subsequent thermal chemistries on Si single-crystal surfaces can be used to generate ordered arrays of novel adspecies, including tetra- σ bonded C2 dimer (>C=C<), di- σ bonded vinylene (-HC=CH-) and vinylidene (>C=CH₂), and mono- σ bonded vinyl (-HC=CH₂) adspecies as well as their chlorinated homologs. We also show that purification of one of these C=C containing arrays could be achieved by simple manipulation of the annealing temperature or by post-exposure of H atoms. * Work supported by the Natural Sciences and Engineering Research Council of Canada.

11:20am **SS2-ThM10 Infrared Spectroscopy Study of Adsorption of Maleic Anhydride on Si(100)**, Y. Kimura, H. Ishii, M. Niwano, Tohoku University, Japan

The adsorption of maleic anhydride on Si(100)-2x1 has been investigated using infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry. Previously, it has been suggested on the basis of HREELS data that at low coverages the adsorption of maleic anhydride occurs through cycloaddition of the C=C bond to the dangling bonds of Si-Si dimers, and at high coverage, maleic anhydride dissociatively adsorbs on the Si(100) surface. In the latter case, the dissociated hydrogen is bound to the Si surface atoms to form the Si-H bond, and the remaining fragments are bound to the Si surface atoms via a single Si-C linkage with retention of C=C double bond. In this study, we observe that an intense absorption peak appears at 2125 cm⁻¹, while the peak due to the C=O stretching vibration is relatively weak. Previously the 2125-cm⁻¹ peak has been assigned as being due to the Si-H stretching vibration mode. However, this peak is positioned at a slightly higher frequency than the monohydride peak that shows up around 2080 cm⁻¹. Furthermore, we observe that the 2125-cm⁻¹ peak appears even when the Si(100) surface is dosed with deuterium-substituted maleic anhydride. From these observations, we suggest that upon adsorption the five-membered ring of maleic anhydride is broken to generate the C=C=O bond and the dissociated molecule is bound to the surface Si atoms via the C-O-Si linkage. Ab initio cluster calculations indeed predict that the C=C=O bond exhibits a vibration mode around 2120 cm⁻¹.

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The present results indicates that maleic anhydride dissociatively adsorbs on the Si(100) surface in a rather complicated manner.

11:40am **SS2-ThM11 Formation of Unsaturated Hydrocarbon Moieties on Hydrogen-terminated Si(111) by Grignard Reaction**, *T. Yamada*, *K. Shirasaka*, *M. Noto*, *H.S. Kato*, RIKEN, Japan; *M. Kawai*, RIKEN and The University of Tokyo, Japan

Unsaturated hydrocarbon moieties, such as $\text{CH@SUB 2@=CHCH@SUB 2@-}$, CH::C- , $\text{CH@SUB 3@CH=CHCH@SUB 2@-}$ and CH@SUB 2@=CH- was deposited on hydrogen-terminated H:Si(111) by using the corresponding Grignard reagents ($\text{C}_x\text{H}_y\text{MgBr}$ or $\text{C}_x\text{H}_y\text{MgCl}$) dissolved in tetrahydrofuran, followed by rinsing in CF@SUB 3@COOH solution. The product adsorbates were examined by vibrational methods with HREELS and internal multiple infrared reflection-absorption spectroscopy. It is anticipated that the unsaturated bonds within moieties may directly react with H:Si(111)@footnote 1@ and may be destroyed besides the desired bond shifting of C-Mg to C-Si. The $\text{CH@SUB 2@=CHCH@SUB 2@:Si(111)}$ adsorbate was detected as the H-C= stretching and out-of-plane bending signals after the reaction in $\text{CH@SUB 2@=CHCH@SUB 2@MgBr/THF}$ at 35°C for 5 min. The uptake of hydrocarbon moieties was 10% of surface Si with the remainder of originally terminating H atoms. The existence of C-Si stretching signal was revealed by using D:Si(111). Similarly in the cases of CH::C- and $\text{CH@SUB 3@CH=CHCH@SUB 2@-}$, the unsaturated bonds were reserved. The double bond within CH@SUB 2@=CH- adsorbate was never observed, presumably because the C=C part would be close enough to the H-Si sites to undergo the direct adsorption. A notable result for better understanding of mechanism is that Grignard deposition just need one single H-Si site with no need for adsorption of MgX species in all cases. This was examined by isotope labeling in the rinsing procedure. Reservation of unsaturated bonds provides an approach to functionalized hydrocarbon moieties by addition reactions. Addition of NH@SUB 2@- , OH- or -COOH groups is prospective in surface modification with biochemical polymers with well-controlled adsorbate structure.@footnote 2@ @FootnoteText@ @footnote 1@M. R. Linford et al., J. Am. Chem. Soc. 117 (1995) 2145.@footnote 2@T. Yamada, et al., J. Chem. Phys. 121 (2004) 10660.

Surface Science

Room 203 - Session SS3-ThM

Reactivity of Bimetallic Surfaces

Moderator: R.A. Bartynski, Rutgers University

8:20am **SS3-ThM1 Temperature Effects on the Nucleation and Growth of Ag Films on 5-fold Surfaces of Icosahedral Al-Pd-Mn Quasicrystal**, *B. Unal*, Iowa State University; *T.A. Lograsso*, *A.R. Ross*, The Ames Laboratory; *C.J. Jenks*, *J.W. Evans*, *P.A. Thiel*, Iowa State University and the Ames Laboratory

Growth of thin films on surfaces of complex intermetallics, such as quasicrystals, can provide new insights into nucleation, growth, and the thermodynamic factors that control film structures. We have used scanning tunneling microscope to study the growth and nucleation of the first few monolayers of Ag on the fivefold surface of an icosahedral Al-Pd-Mn quasicrystal surface at different temperatures. While Ag films grow layer by layer at 127K and 200K, the growth mode switches at about room temperature. Between 300 and 365 K, the Ag segregates in islands that are 4 and 5 monolayers high, on the terraces. When the temperature reaches 420K, islands grow at the step edges rather than on the terraces. This behavior will be discussed in terms of the existence of different types of diffusion barriers on the quasicrystal surface.

8:40am **SS3-ThM2 Pd-Au Model Catalysts: From Planar Surfaces to Nanoclusters**, *K. Luo*, *C.-W. Yi*, *T. Wei*, *D.W. Goodman*, Texas A&M University

Pd-Au bimetallic model catalysts were synthesized as planar surfaces and as well-dispersed alloy clusters on Mo(110) and SiO₂ ultra-thin films, respectively, under ultrahigh vacuum (UHV) conditions. The surface composition, geometric and electronic structures, and CO adsorption properties have been characterized using ion scattering spectroscopy (ISS), X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS), and temperature programmed desorption (TPD). Stable Pd-Au alloy surfaces, where the surface is significantly enriched in Au relative to the bulk, are obtained upon sequential deposition of Pd and Au followed by an anneal. Characteristic isolated Pd sites are identified on the Pd-Au planar and supported Pd-Au clusters. Ethylene adsorption and dehydrogenation show a clear structure-activity correlation with respect to these Pd-Au model surfaces.

9:00am **SS3-ThM3 Site-Directed Chemistry at Pt-Sn Alloy Surfaces**, *B.E.*

Koel, University of Southern California

INVITED

Achieving higher activity and selectivity of heterogeneous catalysts, electrocatalysts, and sensors requires advances in controlling structure and chemistry relevant to interfacial reactions at the nanoscale. One can now exploit an unprecedented ability to investigate such phenomena on alloy surfaces to obtain new information about how and why composition, structure, and defects alter chemical reactions that occur at specific sites. We have been probing this site-directed chemistry at alloy surfaces in a wide range of chemisorption and catalytic reactivity studies. The talk today will focus on how recent results for several Sn/Pt(111) and Sn/Pt(100) ordered surface alloys have helped to define the overall chemical reactivity of Pt-Sn bimetallic surfaces, clarified the role of a second metal in altering the chemistry of Pt alloys, and led to general principles for understanding the reactivity and selectivity of alloy catalysts. Specifically, I will discuss exploiting Pt-Sn alloys for selective hydrogenation of 1,3-butadiene based on studies of well-defined model catalysts, i.e., Pt(111) and the (2x2)-Sn/Pt(111) and (sr@3x@sr@3)R30°-Sn/Pt(111) surface alloys, that probe the influence of alloyed Sn on the reaction barrier to butadiene hydrogenation and the effect of surface Sn concentration on hydrogenation activity and selectivity. Fundamental concepts emerging from such studies enhance our understanding and ability to tailor local properties of alloy surfaces, which should facilitate the design of new catalysts and sensors.

9:40am **SS3-ThM5 Probing Complex Adsorption Structures: A Joint Experimental and Theoretical Study of Prenal Adsorbed on Pt(111) and Pt-Sn Surface Alloys**, *J. Haubrich*¹, University of Bonn, Germany; *D. Loffreda*, *F. Delbecq*, *P. Sautet*, Ecole Normale Supérieure de Lyon, France; *A. Krupski*, *C. Becker*, *K. Wandelt*, University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of @alpha@.@beta@-unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. Although numerous studies have been dedicated to systems like acrolein or prenal on Pt(111) in recent years, the details of the molecule-surface bonding still remain under debate. Yet the selectivities of such processes depend crucially on the adsorption complexes. Their characterization is even more complicated when alloy surfaces are considered because alloying is often used to optimize the properties of the catalyst. We here present a joint experimental and theoretical study on molecule-surface bonding of prenal on Pt(111) and two Pt-Sn surface alloys based on the interpretation of HREEL spectra using ab initio density-functional theory (DFT). Additionally TPD and LEED studies of prenal adsorbed at 100K on these surfaces were performed. While on Pt(111) the desorption of prenal is detected at 160K (multilayer) and 199K, also fragmentation reactions are observed giving rise to desorption of H@sub 2@ and CO. On Pt@sub 2@Sn and Pt@sub 3@Sn/Pt(111) this fragmentation process is suppressed. The HREELS experiments were carried out between 100K and 500K on Pt(111) show highly complex spectra of the adsorbed prenal and its fragments, which can be detected above 300K. On both Pt-Sn surface alloys very similar HREEL spectra of prenal are recorded. Combining the HREEL spectra with the results of the vibrational analysis obtained from the DFT calculations, we are able to identify stable adsorption geometries, interpret the normal modes corresponding to the measured loss peaks and to point to likely reaction intermediates.

10:00am **SS3-ThM6 Catalytic CO Oxidation at 70 K on a Au/Ni Surface Alloy**, *D.L. Lahr*, MIT; *S.T. Ceyer*, MIT, US

A Au/Ni surface alloy catalyzes the oxidation of CO at low temperature by at least three distinct mechanisms. At the lowest temperature of 70 K, molecularly adsorbed O@sub 2@, spectroscopically characterized by high resolution electron energy loss spectroscopy as peroxy or superoxy species bound at multiple sites with vibrational frequencies of 865 and 950 cm@sup -1@, are the reactants with CO. A third molecularly adsorbed O@sub 2@ species, characterized by an O-O stretch mode at 790 cm@sup -1@, does not react with CO. Between 105-125 K, CO@sub 2@ production coincides with O@sub 2@ dissociation, suggesting a "hot atom" mechanism in which an O atom, formed upon dissociation of adsorbed O@sub 2@, reacts with CO before equilibrating with the surface. The CO that reacts is characterized by a C=O stretch mode at 2170 cm@sup -1@. Given the relatively high frequency, the reacting CO is likely bound to a Au atom. Above 125 K, CO bound to Au reacts with atomically adsorbed O atoms, characterized by a O-Au stretch mode at 660 cm@sup -1@. These results show that nanosize Au clusters bound to oxide supports are not a

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¹ Morton S. Traum Award Finalist

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necessary condition for Au catalyzed, low temperature CO oxidation. In addition, the lower temperature at which the CO oxidation reaction occurs on the Au/Ni surface alloy as compared to the reaction temperature (~200 K) on the supported Au nanoclusters demonstrates that the activation energy is significantly lower on the Au/Ni surface alloy than on Au nanoclusters.

10:20am **SS3-ThM7 The Chemical Properties of Pd-Au Alloy Surfaces**, *T. Wei, J.H. Wang, C.-W. Yi, D.W. Goodman*, Texas A&M University

The chemisorptive behavior of CO on Pd-Au alloy films and silica-supported Pd-Au nano-clusters has been studied by infrared reflection adsorption spectroscopy (IRAS). The relative influence of geometric versus electronic effects has been addressed by comparing the alloy and single component surfaces. A unique CO vibrational feature at 2088 cm^{-1} , corresponding to CO adsorbed on isolated Pd sites on Au, is clear evidence of an ensemble effect. On the other hand, the IRAS data for CO adsorbed on Pd-Au alloy surfaces show no evidence for an electronic effect of Au on Pd. The surface concentration of isolated Pd sites can be controlled by systematically altering the Pd-Au alloy composition, allowing detailed studies of isolated Pd sites as active sites for adsorption and reaction.

10:40am **SS3-ThM8 Unoccupied Electronic Structure and CO Adsorption in Ni/Cu(100) System**, *H. Yao, S. Rangan, A.G. Danese, R.A. Bartynski*, Rutgers University

Ultrathin (i.e. several monolayers thick) metal films in the nanometer thickness range exhibit quantum size effects in their electronic structure. These effects often lead to interesting magnetic, optical or chemical properties. The particular materials selected in our work here Ni/Cu(100) system are motivated by two main reasons: First, because its applications in spin valve structures; second, we would expect that the study of this system will help us to understand the anomalous downward dispersion of unoccupied states in Cu/Ni/Cu(100) systems. We performed a series of inverse photoemission (IPE) studies of the unoccupied electronic structure of the Ni/Cu(100) and CO/Ni/Cu(100) systems as a function of Ni thickness. IPE spectra from Ni films exhibit very rich structures. A phase accumulation model (PAM) calculation suggests only one of the three main features is consistent with metallic quantum well (MQW) State in Ni film. CO adsorption strongly modifies the spectrum by dramatically suppressing one of the main features indicating that this feature is a Ni surface resonance. Furthermore, by comparing spectra from Ni/Cu(100) with results from Cu/Ni/Cu(100), we suggest the third feature is a state confined to the Ni/Cu interface, and the Cu/Ni interface state plays key roles in the anomalous dispersion of the unoccupied states in the Cu/Ni/Cu (100) system. The correlation between chemisorption properties of Ni films of different thickness and their electronic structures are studied with Temperature Programmed Desorption (TPD) and IPE. First principles calculations illustrating the evolution of the electronic structure of Ni/Cu structures as a function of both Ni and Cu film thickness will also be presented and compared to the experimental measurements.

11:00am **SS3-ThM9 Atomically and Time Resolved Pattern Formation in Strained Metal Films: S on Submonolayer Ag/Ru(0001)**, *B. Diaconescu*, University of New Hampshire, US; *K. Pohl*, University of New Hampshire

Strained metallic interfaces can lead to highly ordered misfit dislocation networks that can be utilized as a bottom-up patterning method for the growth of cluster arrays of specific size and density. The great potential of this natural templating method is that the characteristic length scales are predicted to depend on the interfacial stress. 2D sulfur cluster growth on the misfit dislocation network of submonolayer Ag on Ru(0001) relaxes the 6nm x 4nm unit cell of the strained Ag film into a large-scale ordered triangular array of S filled vacancy islands, 5nm apart. Variable Temperature STM and LEED studies reveal that 2D S cluster growth takes place in two regimes: (1) At low S coverage a dilute phase of S clusters, etched at the threading dislocation sites of the Ag film forms. S clusters have an average size of 1.5nm corresponding to two S atoms per cluster, and a highly temperature dependent mobility. (2) At a S coverage above 0.018 ML the solid S cluster phase forms after all the available threading dislocation sites of the Ag film were etched. In this regime the highly ordered S cluster array shows a S coverage dependent cluster size and a $\sqrt{2} \times \sqrt{2}$ S/Ru(0001) structure. In the growth process S partially relieves the strain in the Ag film as seen by the relaxation of the misfit dislocation network. For S coverage beyond 0.33 ML on the Ru(0001) terrace, the compressed S phase pushes Ag atoms into the second layer and the ordering of the S clusters is partially destroyed. It is found that exchange-induced inhomogeneous nucleation of S adatoms modifies the interfacial stress in the submonolayer Ag/Ru(0001) film and, that the size of

the S-filled vacancy islands in the ordered self-assembled array can be controlled with S coverage. @FootnoteText@ @footnote 1@ K.Pohl et al. Nature 397, 238 (1999)@footnote *@ Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

11:20am **SS3-ThM10 Experimentally and Theoretically Determined Core-Level Shifts for Ultrathin Pd, Ag and AgPd Films on Ru(0001)**, *J. Onsgaard, L. Bech*, Aalborg University, Denmark; *W. Olovsson*, Uppsala University, Sweden; *I. Abrikosov*, Link@um o@ping University, Sweden

Ultrathin composed metal films deposited on a relatively inert substrate are complex systems that are subject to both thin-film and surface-alloying effects. The evolution during build-up of ultrathin films of Pd and/or Ag deposited on Ru(0001) was followed by means of synchrotron-based photoelectron measurements (PES) of the valence band and of the Pd and Ag 3d5/2 core levels. Similarly, the evolution during stepwise annealing of ultrathin films of Ag and Pd deposited one-by-one on Ru(0001) was followed. LEED was applied to gain information on the atomic structure. The sample temperature was close to room temperature during data acquisition, whereas it typically was kept at ~550 K during metal exposures. Characteristic changes observed during film growth and annealing will be demonstrated. Further, experimentally obtained core level PES measurements will be compared with results of Density Functional Theory (DFT) calculations, which are based on the coherent potential approximation (CPA) and carried out within the complete screening picture, which includes both the initial and final state effects of PES.

11:40am **SS3-ThM11 The Photoemission Study of Oxygen Adsorbate on Pt@sub 3@Ni (100), (110), and (111) Surfaces**, *B.S. Mun*, Lawrence Berkeley National Laboratory, US; *M. Watanabe, M. Rossi, V. Stamenkovic, N.M. Markovic, P.N. Ross*, Lawrence Berkeley National Laboratory

The electronic structures of oxygen covered surfaces on Pt@sub 3@Ni (100), (110), and (111) alloys are studied with photoemission spectroscopy. The positions of local d-band center and the widths from valence band density of state (DOS) measurements are compared before and after the oxygen adsorption at various temperatures. The correlations between the electronic structures of oxygen-adsorbed surfaces and the chemical properties are discussed. Modified electronic structures of Pt@sub 3@Ni surfaces are also compared to those of Pt single crystals surfaces. The density functional theory calculation is carried out for the comparison of the experimental results to the theory.

Surface Science

Room 202 - Session SS1-ThA

Transport and Structural Stabilization of Surfaces

Moderator: L. Bartels, University of California at Riverside

2:00pm **SS1-ThA1 Living on the Edge: Life and Death of Vacancies in Cu(100)**, *K. Schoots, M.J. Rost, J.W.M. Frenken*, Leiden University, The Netherlands

We have used STM to investigate where surface vacancies originate and annihilate on Cu(100). Because of the extremely high mobility of the surface vacancies, we have been forced to use tracer particles to follow the vacancy motion, in the form of In atoms, incorporated in the top layer. The "slide-puzzle"-diffusion of the vacancies makes the In atoms move through the surface, as has been reported in.¹⁻³ In the present study, we have employed tailor-made geometries, in which the In atoms were surrounded exclusively by upward or by downward steps. Our STM movies show a striking difference between these two cases, with differences in jump frequencies and average jump lengths of more than one order of magnitude. These results show that vacancies are primarily created at the upper side of a step and can be formulated in analogy with the energetics of ad-atoms, in terms of an Ehrlich-Schwoebel barrier⁴ for surface vacancies. ¹ R. van Gastel et al., Nature 408 (2000) 665, Phys. Rev. Lett. 86 (2001) 1562, Surf. Sci 521 (2002) 10, Surf. Sci. 521 (2002) 26.² M.L. Grant et al., Phys. Rev. Lett. 86 (2001) 4588.³ R. van Gastel et al., The Chemical Physics of Solid Surfaces, vol. 11, Surface Dynamics, ed. D.P. Woodruff, (Elsevier, Amsterdam, 2003), p. 351-370.⁴ G. Ehrlich et al., J. Chem. Phys. 44 (1966) 1039.

2:20pm **SS1-ThA2 Diffusion of Two Dimensional Cu Adatom Islands on Cu(111) using a "Self Learning" Kinetic Monte Carlo Technique**, *T.S. Rahman*, Kansas State University; *O. Trushin*, Russian Academy of Sciences; *A. Kara, A. Karim*, Kansas State University; *P. Vikulov*, Russian Academy of Sciences

Diffusion of two dimensional Cu adatom islands, containing 1 to 100 atoms, on Cu (111) has been studied using a newly developed "self learning" Kinetic Monte Carlo (SLKMC) technique in which the standard KMC method is combined with procedures for automatic generation of a table of microscopic events and calculation of their activation energy barriers. Nontrivial paths thus revealed and fully characterized are permanently recorded in a database for future usage, through a pattern recognition scheme. The system thus automatically builds all possible single and multiple atom processes that it needs for sustained simulation and evolves according to processes of its choosing. The diffusion coefficients calculated for 300K, 500K, and 700K, show that the effective diffusion barriers increase almost monotonically with increasing island size. From the tabulated frequencies of events we find that concerted motion and multiple particle processes play a key role in the diffusion of small islands, however, periphery diffusion and single particle processes dominate for the larger sized islands. Contrary to the case of small Cu islands on Cu (100), we do not find any oscillatory behavior for the effective diffusion barrier or for the diffusion coefficients as a function of island size.

2:40pm **SS1-ThA3 Exclusively Linear Diffusion of 9,10-Dithioanthracene on an Isotropic Cu(111) Surface**, *K.-Y. Kwon, K.L. Wong, G. Pawin, L. Bartels*, University of California at Riverside

One-dimensional diffusion of adsorbates is a common feature of anisotropic surfaces such as the (110) and (211) cuts of an fcc crystal. The technologically-relevant lowest energy (111) surfaces of coinage metals have sixfold symmetry in the top layer and, hence, generally allow diffusion of adsorbates along more than one direction. Here, we report on the diffusion of individual 9,10-dithioanthracene (DTA) molecules on Cu(111). DTA adsorbs with the aromatic system lying flat on the substrate. In variable-temperature STM studies, we find that it diffuses exclusively in the direction in which its aromatic moiety happened to adsorb. We neither find rotation of the molecule in the surface plane nor diffusion perpendicular to the aromatic axis of the molecule. We investigated the dynamics of the one-dimensional diffusion of DTA and find an energy barrier of 130meV and an attempt frequency of 4 GHz. Density Functional Theory modeling of the diffusion potential shows, that DTA achieves unidirectional motion by sequential placement of its two substrate linker in a fashion that strikingly resembles bipedal locomotion.

3:00pm **SS1-ThA4 Bustling Bi/Cu(111): Phase Transitions and Atomic Structure**, *R. van Gastel*, University of Twente, The Netherlands; *D. Kaminski, E. Vlieg*, Radboud University Nijmegen, The Netherlands; *B. Poelsema*, University of Twente, The Netherlands

We have combined surface X-ray diffraction (SXRD) and low-energy electron microscopy (LEEM) to investigate atomic structure and pattern formation in the Bi/Cu(111) system. Deposition of submonolayer amounts of Bi on Cu(111) leads to the formation of a two-phase system consisting of a surface alloy phase and an overlayer phase that forms patterns similar to those previously observed in the Pb/Cu(111) system.^{1,2} The patterns however exhibit several phase transitions that are unseen in Pb/Cu(111). Through SXRD measurements investigating the structure of the different surface phases,³ the origin of these transitions can be pinpointed to changes in the atomic structure of those phases. A rich variety of surface phases, covering the whole spectrum, from solid to liquid to lattice-gas-like and from ordered to disordered is observed. In LEEM movies, structural contrast between e.g. solid and liquid Bi overlayers lets us image the pattern dynamics and phase transitions directly. The pattern dynamics and the dramatic changes that occur during the transitions are analyzed to extract information and quantify the thermodynamic quantities that control the rich phase behavior in this system. ¹ R. Plass, N.C. Bartelt and G.L. Kellogg, J. Phys. Cond. Mat. 14 (2002), 4227.² R. van Gastel, R. Plass, N.C. Bartelt and G.L. Kellogg, Phys. Rev. Lett. 91 (2003), 055503.³ D. Kaminski, P. Poedt, E. Aret, N. Radenovic and E. Vlieg, Surf. Sci. 575 (2005), 233.

3:20pm **SS1-ThA5 Quantum Stabilization of Atomically Flat Films of Pb at 300 K**, *R. Miranda*, Universidad Autónoma de Madrid, Spain **INVITED**

The 1D confinement of electrons within quantum wells produces a set of new states, the quantum well states (QWS), which may influence substantially the electronic energy and, thus, the total energy of the system. Pb grown on Cu(111) shows these effects in the form of "magic heights" for the 3D nanoislands that appear upon deposition at 300K.¹ The "magic heights" are equivalent to the "magic numbers" reported for clusters, He droplets or nuclei. Deposition of Pb at 60 K, however, produces flat, metastable films that cover uniformly the Cu substrate. Their thicknesses can be determined by the characteristic energy of the QWS measured with Tunnelling Spectroscopy. The films grow layer by layer at low temperatures because of kinetic constraints, but upon heating, they decompose into the heights more stable. The dynamics of the thermal evolution of films of different thicknesses is explored by movies recorded with a Variable Temperature STM and compared to electronic energy calculations. We find that each Pb thickness becomes unstable at a different temperature (with films with QWS at the Fermi level (such as 9 ML-thick) being particularly unstable), while layers with thickness corresponding to "magic heights" are more stable. Some thicknesses are particularly stable, giving rise to atomically flat films of Pb over micron scales even at room temperature. ¹R. Otero, A.L. Vazquez de Parga and R. Miranda, Phys. Rev. B 55, 10791 (2002).

4:00pm **SS1-ThA7 Atom Transport in One-Dimensional Surface Diffusion**, *G. Antczak, G. Ehrlich*, University of Illinois at Urbana-Champaign

We present an investigation of self-diffusion on the W(211) plane, done using atomic resolution field ion microscopy, which gives insight into the mechanism of migration of atoms in a one-dimensional system. We distinguish two temperature regions in diffusion over this surface. A low temperature region, where diffusion proceeds by the standard, well-known mechanism - jumps to nearest-neighbor sites, and a slightly higher temperature region, where double transitions start to play a significant role. The transition between these two regions is gradual. The existence of double jumps starts to be non-negligible at a temperature $T = 310$ K and the ratio of double to single transitions reaches 0.66 at a temperature $T = 325$ K. The importance of transitions occurring during the transient time is also examined. To get information about ratios of long jumps, the distributions of displacements consisting of 1200 observations for each temperature, is analyzed for regular measurement as well as for transient time measurements. In the lower temperature range, 300 measurements for each temperature are used to establish an Arrhenius plot for the diffusivity. For the first time it is shown that long transitions raise the prefactor for the diffusivity above the usual values. However, this increase is smaller than expected from a model of independent jumps. Activation energies and prefactors for double as well as single transitions are derived. A mechanism of long transitions on W(211) is proposed and compared to

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the mechanism for two-dimensional diffusion on W(110). Research supported by the Department of Energy under Grant No. DEFG02-91ER45439 to the Materials Research Lab.

4:20pm SS1-ThA8 Diffusion and Ordering of CO Coadsorbed with H on Pd(111) Studied by Variable-Temperature STM, T. Mitsui, Lawrence Berkeley National Laboratory; M.K. Rose, E. Fomin, University of California, Berkeley; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

CO adsorbs on Pd(111) in fcc hollow sites at low coverage. As coverage increases, ordered $\sqrt{3}\times\sqrt{3}$ domains form with 1/3 of fcc sites occupied by CO. At higher coverage $c(4\times 2)$ domains form with a density of 1/2, with CO adsorbed in either bridge sites, or in fcc and hcp hollow sites. Additional CO structures are formed at still higher coverage. H also adsorbs on Pd(111) in fcc sites, forming ordered $\sqrt{3}\times\sqrt{3}$ domains with first 1/3 then 2/3 of fcc hollow sites occupied by H. At still higher coverage, H occupies all fcc sites forming 1×1 domains. When H was adsorbed on Pd(111) pre-covered with 0.12 to 0.33 ML of CO, the CO was compressed into $c(4\times 2)$ domains, however higher-density CO domains were not observed even in a constant background pressure of 10^{-7} Torr. Co-adsorption of H has little effect on the diffusion of isolated CO molecules until the H coverage approaches 1/3 ML. At this point the CO diffusivity drops more than two orders of magnitude. CO diffusivity rises significantly as the H coverage passes 1/3 ML, then drops again as coverage approaches 2/3 ML. Very stable CO clusters were observed as H coverage approached 1 ML. Isolated CO molecules could be followed by STM up to ~ 110 K, while isolated CO diffusion on clean Pd(111) can be observed by STM as low as 45 K, and becomes too fast to follow by ~ 55 K. In small clusters CO molecules occupy both fcc and hcp sites, and diffusivity is a dramatic function of cluster size. 2 and 4 molecule clusters diffuse significantly faster than 1, 3 or 5 molecule clusters, and cluster diffusivity generally increases with size up to at least 7 CO molecules. The implications of these observations for inter-adsorbate interactions will be discussed. @FootnoteText@ @footnote 1@ M. K. Rose et al, Surface Science 2002, T. Mitsui et al, Surface Science 2003, T. Mitsui et al, Phys. Rev. Lett. 2005.

4:40pm SS1-ThA9 Sintering of Au Clusters Supported on TiO₂(110): An In-Situ Scanning Tunneling Microscopic Study, F. Yang, Texas A&M University; A. Kolmakov, University of California at Santa Barbara; A.K. Santra, Halliburton Company; D.W. Goodman, Texas A&M University

Sintering, i.e. an increase in the average size of nanoclusters, is a frequently encountered problem in nanotechnology and a principle cause of deactivation in nanocatalysts. For example, Au supported on high-surface-area titania is a highly efficient catalyst for selective oxidation and hydrogenation reactions; however, commercial development is seriously hampered because Au nanoclusters sinter rapidly. The mechanisms of sintering are not well understood and depend, to a large extent, on understanding elementary surface diffusion processes. Scanning tunneling microscopy (STM) is capable of atomic-level measurements over a variety of conditions. In-situ STM allows the morphological changes of specific nanoclusters to be monitored over a variety of reaction conditions from ultrahigh vacuum to realistic reactant pressures. Using in-situ STM, the growth kinetics of Au on TiO₂(110) have been measured directly, allowing sintering mechanisms to be proposed for supported Au model catalysts under realistic reaction conditions. The STM results also show that substrate hydroxylation blocks the preferential growth of Au clusters and alters their growth kinetics on a TiO₂(110) surface. Furthermore, the sintering kinetics of Au clusters during the CO oxidation reaction have been studied for Au clusters supported on TiO₂(110) and on hydroxylated TiO₂(110).

Surface Science

Room 203 - Session SS2-ThA

Gas-Surface Reaction Dynamics

Moderator: K.W. Kolasinski, University of Virginia

2:00pm SS2-ThA1 Why is Formate Synthesis Insensitive to Copper Surface Structures?, J. Nakamura, University of Tsukuba, Japan; Y. Morikawa, Osaka University, Japan; G. Wang, Nankai University, China

Unique structure sensitivity has been experimentally observed for the formate synthesis from CO and H₂ (CO + 1/2 H₂ → HCOO) on copper surfaces and the reverse reaction of formate decomposition. That is, the reaction rate of formate synthesis and

the activation energy are very similar among Cu(110), Cu(100), and Cu(111), meaning a structure insensitive reaction. On the other hand, the reverse reaction of formate decomposition on copper was a structure sensitive reaction with different activation energies. Also, an Eley-Rideal (E-R) type reaction mechanism has been suggested for the formate synthesis, in which CO molecule directly reacts with adsorbed hydrogen without passing through adsorption of CO. Here, we report the results of ab initio density functional theory (DFT) calculation for the formate synthesis. The DFT-GGA calculation has reproduced adsorption energies and adsorption structure of bidentate formate experimentally measured on Cu(111), Cu(100), and Cu(110), which further reproduces the structure insensitive and structure sensitive features for formate synthesis and formate decomposition, respectively. The structure insensitivity is due to the presence of monodentate formate with similar adsorption energies on Cu(111), Cu(100), and Cu(110), giving a similar energetic pathway from CO + 1/2 H₂ to monodentate formate. The structure sensitive feature for the decomposition of bidentate formate is due to a significant difference in the adsorption energy of bidentate formate depending on the Cu surface structure. The structure insensitivity is due to the E-R type reaction mechanism without passing through adsorption of CO, which enables a similar reaction pathway with similar local structures as revealed in the snapshot for the structural change of intermediates.

2:20pm SS2-ThA2 Experimental and Computational Probes of Transition States on Surfaces, A.J. Gellman, D.S. Sholl, P.P. Ye, X. Li, Carnegie Mellon University

Transition states determine the rates of surface catalyzed reactions, however, direct characterization of surface transition states is challenging. Experimental measurements of substituent effects on reaction barriers have been combined with Density Functional Theory to probe the transition states to the β -hydride elimination in ethoxy groups on Cu(111) and the hydrogenation of alkyl groups on Pt(111). Our results allow us to test the recently advanced proposition that surface reactions with reactant-like (product-like) transition states are relatively sensitive (insensitive) to the nature of the catalyst surface. The barrier to β -hydride elimination in fluorine substituted ethoxy groups increases significantly as a result of fluorine substitution. This is ascribed to a transition state in which the β -carbon atom is cationic with respect to the initial state ethoxy group. Comparison of the experimental values of ΔE^{\ddagger} and the predictions of DFT shows impressive agreement and verifies the predictions based on previous experimental measurements. Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups on the Pt(111) surface and the transition state to β -hydride elimination in alkyl groups on the Pt(111) surface. Co-adsorption of hydrogen with alkyl groups and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated with the field and polarizability substituent constants of the alkyl groups in the form of a linear free energy relationship. This indicates that the α -carbon in the transition state is cationic with respect to the initial state alkyl group and that the reactant has greater charge density on the α -carbon than the transition state.

2:40pm SS2-ThA3 Molecular Beam Studies of Rare Gas and HCl Collisions with Functionalized Self-Assembled Monolayers, B.S. Day, L.R. Fiegand, J.R. Morris, Virginia Tech

INVITED

The research objectives of this work are aimed at elucidating the atomic-scale mechanisms of interfacial bonding, diffusion, and reactions that govern gas-surface interactions on organic surfaces. This challenge is particularly formidable for functionalized organic surfaces where the complicated nature of the interface can result in a broad range of reaction pathways. The approach used in these studies for exploring gas-surface reaction mechanisms combines molecular beam scattering techniques with functionalized self-assembled monolayers. Together with surface analysis instrumentation, these techniques are designed to reveal insight into many aspects of the gas-surface interaction and help develop an atomic-level description of the transformation of reactants into products. This presentation will focus on recent investigations into the dynamics of rare gas and HCl collisions with self-assembled monolayers. Atomic beams of high-energy rare gases are employed to explore the initial gas-surface collision in the absence of reactivity. These studies reveal how the atomic-scale nature of organic surfaces determine the extent of interfacial energy transfer and the path to thermal accommodation. The atom scattering studies are used to help interpret the dynamics of reactive gas-surface

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collisions, such as HCl impinging on a hydroxylated surface. In this work, HCl is directed at OH-terminated self-assembled monolayers to learn about how gas-surface hydrogen-bonding forces influence the dynamics of the collision. Measurements of the HCl energy transfer, residence time, and proton exchange probability have provided new insight into the interactions of HCl with well-characterized hydroxylated surfaces.

3:20pm SS2-ThA5 Gas-Surface Reaction Dynamics of NO on Iron Phthalocyanine Thin Films, S.R. Bishop, N.L. Tran, G.C. Poon, A.C. Kummel, University of California, San Diego

Metallophthalocyanines (MPc) have been proposed for use in chemically sensitive field effect transistor (chem-FET) detectors for the measurement of ambient analytes such as NO@sub x@, NH@sub 3@, and O@sub 3@. However, the adsorption energies and mechanisms of the reaction between these gases and MPc thin films have not been studied. We have investigated the reaction dynamics between NO and monolayer Iron Phthalocyanine (FePc) grown on clean Au(111) surface. The sticking probabilities of 0.11 eV monoenergetic molecular beam of NO were measured on both clean Au(111) and ordered 6x6 monolayer-FePc deposited on clean Au(111) as a function of surface temperature. NO sticking on the Au(111) surface occurs through a precursor-mediated physisorption pathway. In comparison, NO sticking on the FePc film occurs via multiple pathways: direct chemisorption to the metal center and precursor-mediated physisorption. Although the metal center of the molecule accounts for only ~3% of the surface, the direct chemisorption pathway has a sticking probability of ~20%. This suggests that the NO molecules are steered to the reactive metal centers by other portions of the FePc molecule. By using a high translational energy molecular beam, the direct chemisorption pathway will be selectively probed.

3:40pm SS2-ThA6 Extracting the Vibrational Ground State Reactivity of Methane on Ni(111) from Ensemble Averaged Experiments, D.R. Killelea, V. Campbell, A.L. Utz, Tufts University

Beam-surface studies have uncovered key details of the dynamics of methane dissociation on transition metal surfaces. When the measured reactivity is averaged over the population distribution of vibrational states in the beam, the data may obscure the role of individual vibrational states in promoting reaction. Here, we measure the reactivity of CH@sub 4@ beams impinging on a Ni(111) surface. We vary the vibrational energy of the beams by changing the beam source temperature. We model the nozzle temperature effect for these data, and extrapolate to find the reactivity of CH@sub 4@ in its vibrational ground state ($v=0$). Our model predicts that at the low translational energies typical of thermal samples, vibrationally excited molecules account for the majority of observed reactivity.

4:00pm SS2-ThA7 Variable ($T@sub g@$, $T@sub s@$) Measurements of Alkane Dissociative Sticking Coefficients, K.M. DeWitt, L. Valadez, K.W. Kolasinski, I. Harrison, University of Virginia

A novel technique for measuring nonequilibrium dissociative sticking coefficients, $S(T@sub g@, T@sub s@)$, with well-defined gas temperature, $T@sub g@$, and surface temperature, $T@sub s@$, is described, along with its application to activated dissociative chemisorption of CH@sub 4@ and C@sub 2@H@sub 6@ on Pt(111). Microcanonical unimolecular rate theory (MURT) is employed to analyze the sticking coefficients and to extract transition state characteristics. The MURT allows the $S(T@sub g@, T@sub s@)$ sticking to be directly compared to other molecular beam and thermal equilibrium sticking measurements. Interestingly, measured $S(T@sub g@ = 300\text{ K}, T@sub s@)$ for CH@sub 4@ on Pt(111) are several times larger than recent thermal equilibrium measurements, $S(T@sub g@ = T@sub s@)$, on supported Pt nanocrystallite catalysts [J. M. Wei, E. Iglesia, J. Phys. Chem. B 108, 4094 (2004)]. This is a surprising result that runs contrary to the popular notion that dissociative chemisorption should be enhanced at the coordinatively less saturated defect sites that should be more prevalent on the ~2 nm diameter Pt nanocatalysts than on a flat Pt(111) surface.

4:20pm SS2-ThA8 First Principles Resonance Energies and Widths of Ions near Surfaces: N-Body Dynamical Predictions of Charge-Transfer Probabilities for Scattered Ions, K. Niedfeldt, E.A. Carter, Princeton University; P. Nordlander, Rice University

By combining periodic density-functional theory calculations of adsorbate resonance widths and shifts with a many-body dynamical charge-transfer theory, we quantitatively assess charge-transfer rates for ions scattering off surfaces. This method goes beyond previous approaches, which have been limited to modeling metal surfaces with either jellium potentials or finite clusters. We consider Li⁺ scattering off Si(001), Mg(0001), Cu(001), and

Al(001). When compared to experimental neutralization fractions for Li ion scattering off of Al(001), our method yields trends in neutralization as a function of scattering angle in better agreement than those derived from jellium models. Our results comparing Mg and Cu show that scattering off of Mg and Cu yield distinctly different charge-transfer probabilities. By contrast, jellium predicts identical scattering properties due to identical theoretical free-electron gas values. As expected, for Li ions scattering off Si(001), the Li 2s orbital interacts most strongly with the Si dimer dangling bonds. The charge-transfer rates for Li ions scattering off Si(001) exhibits extreme variations with lateral position, in contrast again to the jellium picture. Taken together, these results clearly indicate that more realistic ion-surface interaction models (such as provided here) are necessary to obtain even qualitatively correct trends in charge-transfer for many ion-surface interactions.

4:40pm SS2-ThA9 Formation of Multiply Charged Ions by Direct Recoil, X. Chen, Z. Sroubek, J.A. Yarmoff, University of California, Riverside

Low energy ions that impact a solid surface can remove material by sputtering, which produces low kinetic energy particles through a collision cascade, or direct recoil (DR), which involves the emission of a relatively high-energy particle following a hard collision between the incident ion and a surface atom. An inner-shell promotion that places one of the atoms into an excited state is a possible consequence of the hard collision. In these experiments, we find a unique process in which the DR particle is emitted with two holes, i.e., as a doubly charged ion. Si@super +@ ions were incident on atomically clean Al(100). The absolute ionization probability of scattered Si and recoiled Al were measured with time-of-flight, while detailed spectra of the ion yield were collected with an electrostatic analyzer. All of the scattered Si were neutralized, as expected due to its large ionization potential. Spectra collected of the DR Al show, however, a combination of Al@super 1+@, Al@super 2+@ and Al@super 3+@ ions. The multiply charged ions are attributed to a charge promotion of the Al 2p during the hard collision. The Al 2p level is promoted above the Fermi energy by interaction with the Si 2p level that lies just below, such that both electrons are transferred to the solid forming Al ions with two holes. Subsequently, some of the Al@super 2+@ may decay to Al@super 3+@ via autoionization, or pick up an electron to form Al@super 1+@. This mechanism is verified by the observation of an energy threshold for the process, and by spectra of the electrons emitted as the excited states decay. This process of producing multiply charged DR ions is highly effective because of the small separation between the Al and Si 2p levels. Thus, it is expected that similar behavior would occur for other closely matched systems that will be investigated, such as P ions incident on solid Si.

Biomaterial Interfaces

Room 311 - Session BI+SS-FrM

Biomaterials Surface Characterization

Moderator: S.L. McArthur, University of Sheffield, UK

8:20am **BI+SS-FrM1 Charge Injection Barriers and Gap States at the L-Cysteine/Au Interface**, *M.M. Beerbom, R. Gargagliano, R. Schlaf*, University of South Florida

Protein/inorganic materials interfaces are interesting for many bio-engineering applications such as bio-sensors or molecular electronic devices. L-cysteine is particularly interesting since it can form self-assembled monolayers on gold due to its thiol-group. In our experiments we investigated the L-cysteine/Au interface using x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) in combination with a multi-step deposition procedure. PE-spectra obtained after each deposition step yielded a data set allowing the determination of charge injection barriers at the interface, as well as the characterization of the chemical interaction. The L-cysteine deposition was carried out in a glove box directly attached to the PES system enabling contamination-free measurements. Our results indicate the formation of an interface state within the HOMO-LUMO gap due to the thiol-Au interaction. @footnote 1@ This is supported by control experiments on L-cysteine/graphite interfaces, which did not show the formation of this gap state. @FootnoteText@ @footnote 1@M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", *Langmuir Articles ASAP*, (2005).

8:40am **BI+SS-FrM2 Injection into Vacuum and Alignment of Biological Molecules for Electron Diffraction**, *D. Starodub, R.B. Doak, J.C.H. Spence, U. Weierstall, K. Schmidt, G. Hembree*, Arizona State University

Resolving the protein secondary structure (folding), critical for its functionality, is a demanding task, especially for the proteins, which cannot be easily crystallized. Recently it was proposed to collect diffraction patterns dynamically from an array of biological molecules embedded in submicron water droplets, consecutively traversing the intersection of a focused 50 keV electron beam and a polarized 100 W laser beam. @footnote 1@ The latter aligns the molecules due to field interaction with a dipole moment induced in the molecule with anisotropic polarizability tensor. @footnote 2@ We show experimental results on generation of monodispersed microdroplets via growth of Rayleigh instability, their injection into high vacuum, evaporation and cooling. The limitations on the droplet size and temperature for a given jet source configuration are obtained. Rotational relaxation of the spherical (small protein) and rodlike (tobacco mosaic virus) biomolecules to thermal fluctuations about the equilibrium orientation is considered in viscous and free molecular flow regimes, and optimal conditions for alignment, sufficient to obtain sub-nanometer resolution in diffraction, are derived. We also consider adiabatic effects of different spatial profiles of laser beam intensity and droplet velocity on final oscillation states of a biomolecule. Supported by NSF funding SGER DBI-0429814. @FootnoteText@ @footnote 1@J.C.H. Spence and R.B. Doak, *Phys. Rev. Lett.* 92, 198102(2004). @footnote 2@J.C.H. Spence, K. Schmidt, J. Wu, G. Hembree, U. Weierstall, R.B. Doak, P. Fromme. *Acta Cryst.* A61, 237(2005).

9:00am **BI+SS-FrM3 Chemical Interaction Analysis of Adhesive Biomaterial-Hard Tissue Interfaces**, *Y. Nakayama*, Toray Research Center, Inc., Japan; *Y. Yoshida, K. Suzuki*, Okayama University Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Japan; *B. Van Meerbeek*, Catholic University of Leuven, Belgium

Adhesion to human hard tissue plays an important role in both dental and orthopedic therapies. Synthesized adhesive biomaterials made of polymer, as well as of functional monomer, have been developed. Among such adhesive biomaterials, those capable of forming chemical bond with hard tissue such as dentin, enamel or hydroxyapatite (HAp) are more appreciated for achieving more durable adhesion. Evidence of chemical bonding at biomaterial-hard tissue interfaces was recently reported for interfaces between polyalkenoic acid and enamel or HAp with the use of high resolution X-ray Photoelectron Spectroscopy (XPS). @footnote 1@ Preparation of ultrathin biomaterial molecular layer on enamel or HAp substrate enabled high resolution XPS spectrum to distinguish carboxylic carbons with chemical bond to HAp from those without chemical bond at the interface. Chemical interaction of carboxylic acids with HAp was analyzed and adhesion-decalcification concept (AD concept) was

proposed. @footnote 2@ According to the AD concept, the less soluble the calcium salt of the acidic molecule, the more intense and stable the molecular adhesion to a hydroxyapatite-based substrate. Subsequently, adhesive performance of functional monomers, such as those containing dihydrogen phosphate or carboxylic acid, with HAp and dentin was studied. @footnote 3@ In this presentation, we will report chemical interaction analysis of functional monomer-hard tissue interfaces by utilizing high resolution XPS and relating analytical data. @FootnoteText@ REFERENCES: @footnote 1@ Y. Yoshida, B. Van Meerbeek, Y. Nakayama, J. Snauwaert, L. Hellemans, P. Lambrechts, G. Vanherle, K. Wakasa: *J. Dent. Res.*, 79, 709 (2000). @footnote 2@ Y. Yoshida, B. Van Meerbeek, Y. Nakayama, M. Yoshioka, J. Snauwaert, Y. Abe, P. Lambrechts, G. Vanherle, M. Okazaki: *J. Dent. Res.*, 80, 1565(2001). @footnote 3@ Y. Yoshida, K. Nagakane, R. Fukuda, Y. Nakayama, M. Okazaki, H. Shintani, S. Inoue, Y. Tagawa, K. Suzuki, J. De Munck, B. Van Meerbeek: *J. Dent. Res.*, 83, 454(2004).

9:20am **BI+SS-FrM4 Evaluation of Residues on Implant Surfaces by X-ray Photoelectron Spectroscopy**, *V. Frauchiger, R. Luginbuehl*, Dr. H.C. Robert Mathys Foundation

Success of modern implants does not depend on the proper material choice only, but also on the surface chemistry and the proper removal of the ubiquitous present surface contaminations. There are many contemporary analytical methods that permit the qualitative and quantitative analysis of picogram amounts, but only a few methods are suitable for a direct assessment without a special preparation of the implants or the chemical extraction of residues. We applied X-ray photoelectron spectroscopy to assess the cleanliness of osteosynthesis plates and hip endoprosthesis implants. In addition, specially designed test coupon surfaces were used to simulate different surface textures. The samples were soiled with exact amounts of two model process adjuvants (MPA). The first one was based on a mixture of organic compounds used in lubricants and cutting fluids while the second one contained inorganic particles used in blasting processes. The cleaning efficacy of an industrial cleaning process in aqueous media and with sonication was tested. Imaging XPS was applied to localize critical contamination on the surfaces and small area analysis was used to identify the organic residues. In addition to XPS, GC-MS and gravimetric analysis were carried out as complementary techniques. Principal component analysis was used to establish a sensitivity at the ng/cm@super 2@ level by calculating the ratio between the bulk implant material and the carbon or other MPA specific elements. Cleaning tests revealed that the organic residues are completely removed upon proper choice of cleaning conditions and detergents. Residual inorganic particles were found on many samples with a blasted surface texture. The particles were removed only by special treatment of the samples.

9:40am **BI+SS-FrM5 Characterisation of Analyte / Matrix Interaction for MALDI / TOF Targets Using Spatially Resolved X-ray Photoelectron Spectroscopy**, *A.J. Roberts, D.J. Surman, S.J. Hutton*, Kratos Analytical Ltd, UK; *M. Resch*, SDG, Germany; *E. Raptakis, O. Belgacem*, Kratos Analytical Ltd, UK

Matrix-assisted laser desorption/ionisation (MALDI) is now an established technique for mass spectrometry of proteins and peptides. Different matrix-analyte preparation protocols have been shown to influence the desorption or ablation process resulting in either high or low metastable fragmentation. It has been speculated that following laser ablation the velocities of the analyte and matrix can be regarded as a valuable and meaningful characteristic of the MALDI process. However, the interaction and distribution of the analyte with respect to the matrix is poorly understood. Here we present a study of the distribution of a fluorinated peptide as a function of matrix material using imaging x-ray photoelectron spectroscopy (XPS). Both the lateral and depth distribution is investigated to draw conclusions on the incorporation of the analyte in the matrix.

10:00am **BI+SS-FrM6 In Situ Sum Frequency Generation Characterization of Adsorbed Alpha-helical Peptides**, *N.T. Samuel*, University of Washington; *K. McCrea*, Polymer Technology Group; *L.J. Gamble*, University of Washington; *R.S. Ward*, Polymer Technology Group; *D.G. Castner*, University of Washington

Controlling and characterizing the structure of adsorbed biomolecules is important for applications in diagnostics, tissue engineering and nanobiotechnology. Our previous studies showed that peptides with well-defined sequences of lysine (K) and leucine (L) amino acids spontaneously adsorb onto hydrophobic substrates with an alpha-helix secondary structure. The present study characterizes the adsorption of the LK peptides onto the surface through two approaches - immersing the

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hydrophobic substrate through the air-water interface (AWI) and avoiding the AWI. When the LK peptide is adsorbed avoiding the AWI a time-dependent change in the amide I intensity is observed. However, X-ray Photoelectron Spectroscopy (XPS) analysis showed no significant time dependence of the nitrogen surface composition. Similarly, the CH region of the SFG spectrum shows no time-dependence. These results indicate that the amide I SFG spectrum follows the time-dependent ordering of the peptide molecules on the hydrophobic surface. Results from site-specific labeling of the alpha-helix LK peptide molecules with deuterated leucine residues showed it was possible to follow interactions of one amino acid residue of the peptides with the surface.

10:20am BI+SS-FrM7 Molecular Level Studies on Interfacial Protein and Peptide Structures Using SFG, Z. Chen, University of Michigan

Molecular structures of interfacial proteins and peptides play important roles in biocompatibility, anti-biofouling control, membrane protein function, and anti-microbial peptide behavior. Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular structures of proteins and peptides at the solid/liquid interface in situ. A thin film model was adopted to interpret SFG spectra. Isotope labeled method was introduced in the SFG studies. SFG results demonstrate that C-H stretching and amide signals can elucidate structures of hydrophobic side chains and secondary structures of interfacial peptides and proteins respectively. Detailed correlations between SFG amide I signals and secondary structures of interfacial proteins and proteins have been deduced. Various peptides and proteins including several anti-microbial peptides, albumin, lysozyme, fibrinogen, and factor XII (FXII) have been studied. Time-dependent structural changes of adsorbed proteins at the solid/liquid interface have been monitored. In addition, SFG chiral spectra were collected from interfacial peptides and proteins, which provide additional measurements to determine structures of these proteins and peptides. We also showed that combinations of linear vibrational spectroscopy such as attenuated total reflection Fourier transform infrared spectroscopy with nonlinear vibrational spectroscopic techniques such as SFG and four-wave mixing provide more detailed structure of surfaces/interfaces than that from a single technique.

10:40am BI+SS-FrM8 Using Ellipsometry and Textured Surfaces to Enhance Infrared Response of Adsorbed Biomaterials, D.W. Thompson, J.A. Woollam, University of Nebraska-Lincoln

Infrared spectra are of interest for numerous applications because of the chemical bond information present in the absorption characteristics, but obtaining meaningful infrared spectra from monolayers adsorbed to surfaces can be difficult because of the small amount of material being probed. For instance, it is often of interest to probe adsorbates on a surface after exposure to a protein solution. Use of textured (patterned) surfaces to increase the mass of material sensed is expected to enhance these spectra. Here the infrared ellipsometric enhancement is calculated for a layer of adsorbate on a number of proposed nanostructured surfaces to predict which is most advantageous for obtaining infrared spectra. The approach used here could also be applied to other adsorbates by optimizing the pattern dimensions for different sizes. It also works for visible spectroscopy as long as pattern dimensions are significantly smaller than the wavelength. The effect of using these structures (rods, wells, and trenches) is compared to the response of flat metal or dielectric surfaces over a range of incidence angles of the infrared beam. Predicted sensitivities are based on the calculated effect of adsorbate on intensities in an ellipsometric measurement. Trench structures appear to have significant advantages both in sensitivity and ability to distinguish adsorbed species orientation.

11:00am BI+SS-FrM9 Understanding the Elasticity of Fibronectin Fibrils: A Single Molecule Force Spectroscopy Study, N.I. Abu-Lail, T. Ohashi, R. Clark, H. Erickson, S. Zauscher, Duke University

Although fibronectin (FN) is considered to be one of the most important components of the extracellular matrix, the detailed mechanism of the elasticity of FN fibrils is still unknown. To investigate the molecular origin of FN fibril elasticity we performed single molecule force spectroscopy (SMFS) measurements on a recombinant 1-8FN-III protein construct that contained two green fluorescent protein (GFP) domains spliced in-between the 3FN-III and 4FN-III domains. The relative strengths of both domains were investigated over a wide range of pulling rates (50 nm/s to 1745 nm/s). FN-III domains were distinguished from GFP domains based on their characteristic unfolding distance signature. We found that the mechanical stability of both domains was similar and that the unfolding forces of both domains were linearly related to the logarithm of the pulling rate. An

extrapolation of the unfolding forces to small pulling rates showed that the force required to unfold the FN-III domains and GFP domains were undistinguishable and on the order of physiological forces (~10 pN). Our results, combined with earlier fluorescence resonance energy transfer (FRET) studies performed on the same recombinant proteins, suggests (1) that the FN-III domains are most likely bent and looped into a compact conformation in the cell culture and (2) stretching extends their conformation while the domains remain mostly folded.

11:20am BI+SS-FrM10 Protein-Solvent Interactions in Surface-Grafted ELPs Measured by Single Molecule Force Spectroscopy, A. Valiaev, D.W. Lim, S. Schmidler, A. Chilkoti, S. Zauscher, Duke University

Stimulus-responsive biomolecules attract significant research interest due to their potential applications in areas such as drug delivery, molecular motors and nanoscale sensors. Here we present our results of the conformational and hydration behavior of surface grafted elastin-like polypeptides (ELPs), measured by single molecule force spectroscopy. ELPs are stimulus-responsive polypeptides that contain repeats of the five amino acids Val-Pro-Gly-Xaa-Gly (VPGXG), where Xaa is a guest residue, and undergo an inverse phase transition in response to an environmental stimulus, such as a change in temperature. Our results suggest that single-molecule force spectroscopy can be used to quantify the effect of the type of guest residue, pH or ionic strength on molecular conformation and elasticity. By fitting ELP force-extension data to a freely jointed chain model, using our newly developed data analysis approach, we showed that we can resolve differences in Kuhn segment lengths as small as 0.03 nm; i.e., differences that are about an order of magnitude smaller than those previously reported. The observed force-extension behavior at intermediate and large extensions supports a phenomenological model that describes ELPs as kinetically mobile and disordered macromolecules. Importantly we find that molecular elasticity upon extension arises both from a deformation of the polypeptide backbone and from hydrophobic polymer-solvent interactions. Our observations here agree with recent MD simulations which suggest that hydrophobic hydration of side-chains plays an important role for elasticity and provides the molecular basis for the inverse temperature transition behavior.

11:40am BI+SS-FrM11 Developments of Flexible Tethers to Measure Antibody-Antigen Interactions using AFM, Z. Suo, F. TerÄjn Arce, R. Avci, E. Smith, K. Thiltges, B. Spangler, Montana State University

Functionalization of an AFM tip surface with covalently bound flexible tether molecules is of special interest because such a flexibility is necessary to measure, in a controllable fashion, the receptor-ligand binding events in the physiological environment of the biomolecules. However, the interpretation of the experimental data is often obscured by and confused with the nonspecific binding events between the substrate surface and the so functionalized AFM tip. Effective methods must be developed to eliminate and/or to identify these nonspecific binding events. To achieve these objectives we employed low densities of varying-length poly(ethylene glycol) (PEG) units grafted onto gold-coated AFM tip surfaces. These tethers were covalently linked to the antibodies of interest, in this case anti-cytochrome c. It was necessary to pacify the uncovered portions of the AFM tip in order to block the nonspecific tip-surface interactions. This was achieved by using the flowers-in-the-meadow concept: by mixing a self-assembled monolayers of small molecular size hydroxyl-terminated PEG unit (meadow) with the specifically terminated larger molecular size PEG unit (flower) as described above. AFM force-extension measurements using such a tip conducted on mica substrate covered with cytochrome c resulted in force and length distributions which are consistent with the tether lengths employed. The pH value and the ionic strength of the buffer have considerable influence on the binding events between the AFM tip and the surface covered with cytochrome c. We will present results covering these topics as well as the role of the coupling chemistry between the end terminals of a PEG molecule and the anti-cytochrome c and the AFM tip on the efficiency of antibody-antigen recognition events.

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Surface Science

Room 202 - Session SS1-FrM

Surface Modification through Etching

Moderator: K.T. Queeney, Smith College

8:20am SS1-FrM1 Creating Si Structures from Meso- to Nano-scale via Chemical and Laser-Assisted Methods, *K.W. Kolasinski*, University of Virginia

INVITED

Nanocrystalline porous silicon is created by etching Si in fluoride solutions. The reaction is initiated by valence band holes that are provided by laser irradiation or suitable oxidants. The composition of the fluoride solution can be used both to elucidate the mechanism of etching as well as to control properties of the resulting microporous film. Several new classes of stain etchants - containing some combination of HF, NH_4HF_2 , HCl, HNO_3 , Fe(III), Mn(VII) and water - have been investigated. Once porosified, the films exhibit visible photoluminescence (PL). The peak PL wavelength depends on the etchant composition. Properties of the film, such as morphology, porosity and the PL maximum wavelength, respond to the etchant composition. Of particular interest is the observation of a blue shift in PL, which correlates with an increasingly positive electrochemical potential (E_0) of the oxidant. It is argued that E_0 plays a role much like wavelength in photoelectrochemical etching and that smaller nanocrystals are produced with more positive values of E_0 . Micrometer scale Si pillars are formed by chemically enhanced laser ablation using nanosecond excimer laser irradiation (308 nm, $\sim 3 \text{ J cm}^{-2}$) of Si in the presence of SF_6 . Smaller pillars are formed using femtosecond irradiation (790 or 390 nm, $\sim 1 \text{ J cm}^{-2}$). We can control the initiation of precursor holes by ruling a grating into the Si substrate prior to irradiation. Near-field amplification of the laser intensity enhances the formation of the precursor holes and aligns them parallel to the rule. Continued irradiation leads to the break up of the holes into pillars. The pillars can be thinned and eventually removed by wet chemical etching in aqueous KOH resulting first in ordered arrays of pillars with aspect ratios approaching 10,000 (e.g. tens of microns in length, with $\sim 10 \text{ nm}$ tips) and then macropores. Macropore shape is determined by crystallography and the anisotropy of the wet etchant.

9:00am SS1-FrM3 Optical Second Harmonic Generation as a Diagnostic Tool in Ar⁺ and XeF₂ Beam Etching Studies of Silicon, *J.J.H. Gielis, A.A.E. Stevens, P.M. Gevers, H.C.W. Beijerinck, M.C.M. Van De Sanden*, Eindhoven University of Technology, The Netherlands; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands
Insight into surface and interface properties during plasma etching of micro- and nanostructures is essential to obtain optimal device performance. In this work we study surface and interface processes during etching of Si by implementing the surface and interface sensitive nonlinear optical technique of second harmonic generation (SHG) in a UHV multiple-beam experiment including an Ar⁺ ion gun and a XeF₂ beam. SHG has been applied both spectroscopically and in real-time to study H-terminated Si(100) during ion bombardment and (subsequent) XeF₂ etching using a fs Ti:sapphire laser. Low-energy (50-1000 eV) ion bombardment of c-Si results in a layer of amorphous silicon (a-Si) with a thickness of several nanometers and is expected to create defects such as dangling bonds and strained bonds in this damaged layer. For the applied fundamental photon energy range of 1.35-1.75 eV the SHG signal for c-Si is mainly governed by a two-photon resonance at 3.3 eV related to strained Si-Si bonds in the surface region. This resonance has been characterized before, during, and after ion-induced etching of H-terminated Si(100). It has for example been observed that the resonance at 3.3 eV substantially increases in amplitude during ion bombardment while an additional broad resonance at 3.2 eV seems to emerge. From comparison with spectroscopic ellipsometry studies and by XeF₂ dosing experiments, the former resonance is likely to originate mainly from strained Si-Si bonds at the a-Si / c-Si interface while the latter seems to be related to strained bonds in the a-Si surface region. Prolonged XeF₂ etching of a-Si and c-Si results in an almost complete quenching of the SHG signal, followed by a partial recovery of the SHG signal in which two separate resonances can be distinguished. The dynamics of the spectral SHG signal can aid in understanding the role of strained bonds in the Ar⁺ and XeF₂ etching process of silicon.

9:40am SS1-FrM5 157 nm Laser Interactions with Fused Silica@footnote 1@, *S.R. John, J.A. Leraas, S.C. Langford, J.T. Dickinson*, Washington State University

The F₂ excimer laser, with a wavelength of 157 nm and a photon energy of 7.8 eV, has been shown useful for micromachining a number of technologically useful materials and has potential applications in developing optics, resists, and scanners for DUV lithography. Two materials that have been examined extensively are fused silica and PTFE (Teflon). Little has been done to understand the detailed mechanisms underlying the superior etching behavior of these materials at 157 nm. Here we present a summary of our initial studies. Beginning at fluences well below threshold for plasma formation, we have examined the direct desorption of atomic ions from fused silica surfaces at 157 nm. We used time resolved mass spectroscopy to identify the species and determine their kinetic energies. Both Si⁺ and O⁺ are observed. Prolonged irradiation reduces the emission intensities, consistent with the consumption of defects by the emission process. Molecular dynamics simulations of the silica surface suggest that silicon ions bound at surface oxygen vacancies (analogous to E' centers) provide suitable configurations for emission. Direct emission involving antibonding chemical forces (Menzel-Gomer-Redhead model) are suggested as the origin of the observed kinetic energies. If time permits, results on PTFE will be presented, showing significant neutral and ion emissions (with high kinetic energies). This work was supported by the Department of Energy.

10:00am SS1-FrM6 Ion-induced Initiation of Defects on Graphite at Hyperthermal Beam Energies, *X. Liu, T. Tzvetkov, X.D. Qin, D.C. Jacobs*, University of Notre Dame; *N. Mateljevic, J.C. Tully*, Yale University

Ion beams of O⁺, O₂⁺, and Ne⁺ with incident energy of 5-20 eV are used to etch a Highly Oriented Pyrolytic Graphite (HOPG) surface. The study is focused on the initial stages of defect initiation when well-ordered HOPG is damaged by ion bombardment. The defects generated by the ion beam are observed with ex-situ Scanning Tunneling Microscopy (STM). The density and size of the defects are analyzed as a function of the dose, incident energy, and chemical identity of the ion. Kinetic Monte-Carlo simulations reveal that the probability of an incident ion removing a carbon atom from an intact basal plane are orders of magnitude smaller than removing a carbon atom from a site adjacent to a defect.

10:20am SS1-FrM7 Etching of Carbonaceous Thin Films by Atomic Oxygen: The Influence of Chemical Composition, Substrate Temperature and Gas Phase Environment, *H. Fairbrother, J. Gorham*, Johns Hopkins University

The etching of carbonaceous thin films by atomic oxygen (AO) is an important component of many industrial plasma cleaning and decontamination strategies. AO is also the central species responsible for the degradation of polymers exposed to Low Earth Orbit (LEO). To improve the mechanistic understanding of AO mediated erosion processes, the surface reactions of AO with various carbonaceous thin films have been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). In situ XPS analysis revealed that AO mediated erosion rates with carbonaceous films increase rapidly as a function of substrate temperature. This effect was correlated in part with the thermal stability of the oxidized carbon species produced as intermediates during the etching process. In low pressure plasma cleaning processes surfaces are typically exposed to a variety of reactive species. As an initial step towards identifying the existence and magnitude of co-operative effects between AO and other reactive species contained in plasma discharges results will also be presented on the erosion of carbonaceous thin films exposed simultaneously to AO and low energy (< 100eV) electrons. In these studies XPS analysis will be augmented by AFM studies, using HOPG as a model substrate for carbonaceous films. To identify their suitability as protective coatings for spacecraft vehicles exposed to LEO the surface reactions of AO with amorphous carbon phosphide films have also been examined. In these studies phosphorous incorporation was found to retard the rate of AO erosion due to the formation of a passivating surface layer that contains highly oxidized phosphorous species.

10:40am SS1-FrM8 Consequences of Exposing Ionic Single Crystals to UV Laser Light, keV Electrons, and Low Pressure Water Vapor@footnote 1@, *J.T. Dickinson, K. Kjølgaard, S.C. Langford*, Washington State University

At low pressures, water often does not stick to clean, room temperature surfaces, including surfaces of insulating inorganic materials. Nevertheless sorption, including dissociative sorption, can be strongly enhanced by defects, such as atomic steps, vacancies, and adatoms. We have examined

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the consequences of exposing ionic, single-crystal surfaces simultaneously to energetic radiation (UV photons, keV electrons) and relatively low pressures of water vapor. Dramatic synergisms are observed, presumably due to chemisorption-induced bond weakening. We describe mechanistic studies of this phenomenon, including time-resolved measurements of the response of the radiation-induced particle emission to transients in water pressure (DELTA@P@sub H2O@ 10@super -9@ to 10@super -5@ Pa). Both ion and neutral particle emission rates respond to these transients on time scales of micro- to milli-seconds. We use scanning electron and atomic force microscopies to image the surface modifications associated with this loss of material, beginning with the removal of single atomic layers along step edges and eventually yielding micron-scale pits. We present AFM evidence that material removal is highly localized and defect mediated. We suggest that radiation-induced defects produce atomic-scale structures along steps (e.g., kinks) that peel off when the associated chemical bonds are weakened by sorbed, water-derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented. We also show novel nanostructures produced by exposure to energetic radiation in the presence of water vapor. @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

Surface Science

Room 203 - Session SS2-FrM

Electronic Structure of Surfaces

Moderator: J.G. Tobin, Lawrence Livermore National Laboratory

8:20am **SS2-FrM1 Three-Dimensional Valence Band Structure of WTe@sub 2@**, **T. Ohta**, Lawrence Berkeley National Laboratory/Fritz Haber Institute; **A. Bostwick**, **E. Rotenberg**, Lawrence Berkeley National Laboratory

We report complete valence band structure measurement of tungsten ditelluride (WTe@sub 2@) in 3-dimensions (3D) of k-space by angle-resolved photoemission spectroscopy (ARPES). WTe@sub 2@ is comprised of Te-W-Te layers, and is known to exhibit semi-metallic conduction. Unlike most transition metal dichalcogenide compounds, WTe@sub 2@ has an orthorhombic unit cell. It was previously shown by density-function-theory calculation that WTe@sub 2@ has a metallic band in addition to a semi-metallic band, which is brought about by W 5d and Te 5p bands overlapping near the Fermi-level (E@sub F@). So far, the parallel existence of semi-metallic and metallic bands has not been clearly demonstrated in photoemission experiments due to a complex overlap of W 5d and Te 5p derived states, and because of their k@sub z@ (k perpendicular) dependence near E@sub F@. To shed light on this issue, we have conducted complete 3D band structure mapping of WTe@sub 2@ using synchrotron radiation ARPES. 3D band structure mapping is a powerful tool for investigating the entire electronic structure of a material by visualizing valence band in all three k directions. We have clearly observed the semi-metallic and the metallic bands crossing E@sub F@, and the k@sub z@ dependence of both semi-metallic and metallic bands especially close to E@sub F@. While the semi-metallic band has a slight k@sub z@ dependence, the metallic band appears only near the zone center. We compare our measured 3D band structure to the reported band structure calculation with emphasis on the Fermi surface contour. The semi-metallic conduction can be attributed to the semi-metallic band existing throughout the k@sub z@ direction, whereas the metallic band is limited to the zone center.

8:40am **SS2-FrM2 High Resolution Angle Resolved Photoemission Study of the Electronic Structure of InN(0001)**, **L. Colakerol**, **L. Plucinski**, **S. Wang**, **H.K. Jeong**, **K.E. Smith**, **P. Chen**, **T.D. Moustakas**, Boston University

We report a study of the surface and bulk electronic structure of InN(0001) thin films using high resolution synchrotron radiation excited angle-resolved photoemission (ARPES).@footnote 1@ The InN thin films were grown by plasma-assisted molecular beam epitaxy on c-plane sapphire, and transferred in air to the synchrotron. Samples were cleaned both by annealing in UHV and by cycles of nitrogen ion bombardment followed by UHV annealing. Sharp 1 x 1 hexagonal LEED patterns were observed from the films following either cleaning procedure. Aside from the expected bulk valence band states, we have observed a series of unusual states near E@sub F@, in the bulk band gap, for a narrow range of excitation energies and band momenta. These states are free electron-like, with parabolic dispersion around the surface Brillouin zone center. The number of states observed is a function of annealing temperature, and these states are likely the result of segregation of In metal to the surface. Up to four individual

states are observed, and we associate them with quantum well states due to an In metal overlayer. The states are insensitive to contamination by exposure to 1000 L H@sub 2@, and are not related to intrinsic surface states. Our results are discussed in the context of both the known surface electronic structure of GaN (0001),@footnote 2@ and of charge accumulation at InAs surfaces.@footnote 3@ @FootnoteText@ @footnote 1@ Supported in part by the NSF DMR-0311792, by U.S. ARO 40126-PH, and by U.S. AFOSR. Our spectrometer system is funded by U.S. ARO DAAD19-01-1-0364. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ Y.C. Chao, C.B. Stagarescu, J. Downes, P. Ryan, K.E. Smith, D. Hanser, and R.F. Davis, Phys. Rev. B 59, 15586 (1998).@footnote 3@ L.O. Olsson, C.B.M. Andersson, M.C. Haakansson, J. Kanski, L. Ilver, and U.O. Karlsson, Phys. Rev. Lett. 76, 3626 (1996).

9:00am **SS2-FrM3 Phase Diagram of Cr110 Thin Films Measured by ARPES**, **E. Rotenberg**, **B.K. Freelon**, **S.A. Morton**, **H. Koh**, **A. Bostwick**, Lawrence Berkeley National Laboratory; **K. Rossnagel**, Univ. Kiel, Germany; **A.K. Schmid**, Lawrence Berkeley National Laboratory; **S.D. Kevan**, Univ. of Oregon

INVITED

We report the impact of dimensional confinement on physical properties associated with the spin-density wave (SDW) ground state in chromium. These properties are also of some technological importance since chromium is a common component of thin film magnetic structures. We prepared chromium (110) films of high crystalline quality on a W(110) substrate with a wedge-shaped thickness profile so that the impact of confinement can be systematically studied. We have characterized these films using a combination of low-energy electron diffraction and microscopy as well as high-resolution angle-resolved photoemission spectroscopy. By probing the Fermi surface and the nesting vectors that are relevant to the SDW ground state, we characterized the SDW incommensurability in the film directly, and we find that this incommensurability deviates markedly from the bulk value for thin films at higher temperatures: we find commensurate and incommensurate phases that are separated by nearly continuous transitions. Further changes in the SDW phase diagram arise upon hydrogen adsorption. Our results suggest a simple model to explain the delicate interplay between commensurate and incommensurate phases that involves a balance between SDW stabilization energy and surface and interface energetics.

9:40am **SS2-FrM5 Using Spin Resolved Resonant Photoemission to Probe Electron Correlations in Nonmagnetic Ce**, **S.-W. Yu**, Lawrence Livermore National Lab; **T. Komesu**, University of Missouri-Rolla; **B.W. Chung**, Lawrence Livermore National Lab; **G.D. Waddill**, University of Missouri-Rolla; **J.G. Tobin**, Lawrence Livermore National Lab

We have studied the spin-spin coupling between two f electrons of nonmagnetic Ce by means of spin resolved resonant photoemission. The two f electrons participating in the 3d5/2 to 4f resonance process are coupled in a singlet while the coupling is veiled in the 3d3/2 to 4f process due to an additional Coster-Kronig decay channel. Based on the Ce measurements, it is argued that spin resolved resonant photoemission is a unique approach to study the correlation effects, particularly in the form of spin, in the rare-earths and the actinides.

10:00am **SS2-FrM6 Localized Electronic States Around a Single Kondo Impurity from a First Principles Embedding Theory**, **P. Huang**, **E.A. Carter**, Princeton University

Scanning tunneling microscopy (STM) experiments of a single, magnetic adatom on non-magnetic metal surfaces reveal a sharp resonance in the immediate neighborhood around the adatom [e.g. Manoharan et al., Nature 403, 512 (2000)]. This intriguing observation has been interpreted as the presence of a "Kondo cloud", in which the localized d-electrons on the magnetic adatom hybridize with the metal band states to form an extended open-shell singlet near the Fermi level, thus effectively screening out the impurity moment. While the STM experiments have provided a first atomic-scale glimpse of this surface Kondo state, questions remain about the detailed electronic structure, and the nature of the low-lying excitations which give rise to the Kondo resonance width. We present a first-principles study of the electronic structure of a single Co adatom on Cu(111). Our approach is based on an embedding strategy [Kluner et al., PRL 86, 5954 (2001)], which views the Co adatom and nearest neighbor Cu atoms as a metal cluster embedded in a periodic slab background. The total Co/Cu(111) system is treated using density functional theory (DFT), which allows for a mean-field treatment of an extended periodic system. Using the DFT density for the total system, the effect of the background is cast into an effective embedding potential acting on the cluster. Explicitly-

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correlated theories (i.e. perturbation theory, configuration interaction) are subsequently applied to the embedded cluster in the presence of the embedding potential. The low-lying, many-body excited states are also treated within this same framework to yield excitation energies and wave functions.

10:20am **SS2-FrM7 Persistent Superconductivity in Ultra-Thin Pb Films: A Scanning Tunneling Spectroscopy Study**, *D. Eom*, *S. Qin*, The University of Texas at Austin; *M.-Y. Chou*, Georgia Tech; *C.K. Shih*, The University of Texas at Austin

We report a direct probe of the superconducting order parameter of superconducting crystalline Pb films in the ultra-thin regime (5 -18 ML) by using a home-built low temperature scanning tunneling microscopy/spectroscopy (STM/S). Surprisingly, we find that the 2D Cooper pair condensates remain extremely robust down to the thinnest film (5ML) without any signature of the transition temperature (T_c) suppression. Moreover, we find that the quantum oscillations of order parameter are also very persistent in this regime and the oscillation correlates directly with the density of states (DOS) oscillation at the Fermi level. Finally a constant value of the ratio of energy gap to T_c close to that of the bulk was found, implying the same strong coupling nature for electron-phonon interaction. More detailed analysis of the interplay of quantum size effects and superconductivity will be reported.

10:40am **SS2-FrM8 Surface Electronic Transport in Ultrathin Silicon-on-Insulator**, *P. Zhang*, *E. Tevaarwerk*, *B. Park*, *D. Savage*, University of Wisconsin-Madison; *G. Celler*, Soitec USA; *I. Knezevic*, *P. Evans*, *M.A. Eriksson*, *M.G. Lagally*, University of Wisconsin-Madison

Silicon-on-insulator (SOI), a thin single-crystal silicon template layer on silicon dioxide, promises to become the platform for future high-speed electronics, as well as for a range of sensor technologies. When the Si layer is very thin, unique phenomena arise. The emergence of novel electronic properties with decreasing Si template layer thickness is particularly important. In contrast to the conventional view, ultrathin SOI displays rich electronic phenomena. It is usually claimed that STM imaging of thin SOI is impossible, because a thin SOI layer is fully depleted of free carriers (and thus overly resistive), which in effect eliminates the current path from the STM electrode tip to the contact. In complete contrast to this view, we report successful STM imaging of ultrathin (10 nm) SOI, when the top native oxide is removed and a clean reconstructed Si (001) surface is exposed. We explain theoretically the low sheet resistance of ultrathin SOI that has a reconstructed-Si [(2x1)] surface. We attribute the ability to image to surface electronic transport. The presence of a high density of states in surface bands (π and π^*) and the position of the narrow surface bandgap are the dominant mechanisms in repositioning the Fermi level in ultrathin SOI. They lead to a high density of free carriers. The bulk doping density and the density of interface states on the back Si/SiO₂ interface are largely irrelevant for electronic properties of ultrathin SOI with a clean reconstructed surface. We confirm this conclusion with sheet resistance measurements on SOI covered with thin oxide. The influence of hydrogen on conductivity in ultra-thin SOI will also be discussed. Our measurements suggest that it will be possible to follow thin-Si-membrane structure and properties continuously from bulk to the ultimate limit of a Si film one unit cell high on oxide. Research supported by NSF, AFOSR, and DOE. @FootnoteText@ @footnote 1@Pengpeng Zhang, et al., submitted.

11:00am **SS2-FrM9 Using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS) to Determine the Unoccupied Electronic Structure of Pu**, *M.T. Butterfield*, *J.G. Tobin*, *N.E. Teslich Jr.*, *R.A. Bliss*, *M.A. Wall*, *A.K. McMahan*, *B.W. Chung*, *A.J. Schwartz*, Lawrence Livermore National Laboratory

The investigation of the actinides is of great interest because of their unique electronic structure. At the pivotal point of the behavior of the electronic structure of the actinide series is plutonium. Pu has the most complex phase diagram of all metals, both with regard to the intricacy of the crystal structures and the number of different phases. While there are a number of ongoing experimental efforts directed at determining the occupied electronic structure of Pu, there is essentially no experimental data on the unoccupied electronic structure of Pu. We aim to determine the conduction band (unoccupied) electronic structure of Pu and other actinides in a phase specific fashion and emphasizing bulk contributions by using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS). BIS is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out). IPES can be used to

follow the dispersion of electronic states in ordered samples. Owing to its low energies, IPES is usually very surface sensitive. However, by working at higher energies, we will sample preferentially for bulk properties, downgrading the impact of surface effects, following a philosophy similar to that of Mo et al. @footnote 1@ Thus, from BIS, we would have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu. By using a nano-focused electron source associated with a SEM, we hope to gather phase specific information from crystallites within polycrystalline Pu samples. We will discuss the experimental arrangement required to carry out such an experiment and our progress in building such a system. Acknowledgements :This work was performed under the auspices of the U.S. DOE by University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48. @FootnoteText@ @footnote 1@S.-K. Mo et al, Phys. Rev. Lett. 90, 186403.

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